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AFRPL-TR-69-4

RESEARCH AND ENGINEERING DATA
ON INHIBITED N₂O₄

Final Report

January 1969

Rocketdyne
A Division of North American Rockwell Corporation
Canoga Park, California

TECHNICAL REPORT AFRPL-TR-69-4

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Air Force Rocket Propulsion Laboratory
Research and Technology Division
Edwards Air Force Base, California
Air Force Systems Command
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Dubb, H E

Fisher, J

Neale, B C

Rosengard, J

Axworthy, A

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Air Force Rocket Propulsion Laboratory
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Air Force Systems Command
United States Air Force

FOREWORD

The research reported herein was supported by the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Edwards Air Force Base, California, Air Force Systems Command, United States Air Force, under contract numbers, F04611-67-C-0008, F04611-67-C-0099, and AF 04(611)-10809. Lieutenants R. Fagnoli and D. Huxtable served as Project Monitors. The final reports for F04611-67-C-0008 and F04611-67-C-0099 are presented in the first two sections of this document. A final report, AFRPL-TR-66-320, was issued in January 1967 for Contract AF 04(611)-10809; a supplement to that final report is presented in the third section of this document.

The work described covers the period 1 October 1966 through 15 October 1968. Some of the earlier work under AF 04(611)-10809 is included for comparison. The Responsible Scientist for these programs was Dr. Hubert E. Dubb. Dr. J. Silverman served as Program Manager until 7 January 1967; Dr. K. H. Mueller was Program Manager during the remainder of the effort.

The work was mainly conducted within various organizations of Chemical and Material Sciences (formerly the Chemistry section) of the Research Division. Dr. J. Silverman is manager of Chemical and Material Sciences. The program was conducted by Physical Chemistry which is supervised by Dr. A. E. Axworthy and managed by Dr. K. H. Mueller.

The following additional personnel contributed to this program:

<u>F04611-67-C-0008</u>	<u>F04666-67-C-0099</u>	<u>AF 04(611)-10809</u>
G. Brull	V. Dayan	S. Cohz
J. Fisher	J. Fisher	A. D. Lev
J. Halchak	A. D. Lev	T. Lajcik
J. Lecce	B. C. Neale	H. H. Rogers
A. D. Lev	H. Schultz	J. Rosengard
	J. E. Sinor	R. Rushworth
	M. Stutsman	B. C. Neale

This report has been assigned the Rocketdyne report No. R-7680.

This technical report has been reviewed and is approved.

W. H. EBELKE, Colonel, USAF
Chief, Propellant Division

ABSTRACT

The results are presented for three programs which were conducted to further develop and characterize "inhibited N_2O_4 " (INTO) which is N_2O_4 containing 1 to 3 weight percent FN_2O_2 . The purpose of the fluorine oxidizer is to react with any water which might intrude into the propellant. Long-term corrosion tests were also conducted with "wet" and dry INTO. Stress corrosion tests were conducted with the two current propellant-grade INTO's, MIL-P-26539 and MSC-PPD-2A.

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SUMMARY

It has been demonstrated previously, AFRPL-TR-66-320, that addition of the fluorine oxidizer FNO_2 to NT0 leads to a reduction of the nitric acid and nitrous acid content (formed from water) of the propellant with the concurrent production of HF. It had also been shown that the resulting oxidizer system is storable at 70 C in passivated containers of aluminum, stainless steel, and nickel. The programs reported herein were conducted to further develop and characterize inhibited NT0, INTO (NT0 + 1 to 3 weight percent FNO_2).

The storability of INTO was investigated at ambient and 70C in tanks of 10- to 24-gallon capacity constructed of 347 stainless steel, 1018 carbon steel, 250 maraging steel, 2219 aluminum, 2014 aluminum, and titanium 6Al-4V. An additional feature of these large-tank storability tests was that the FNO_2 was prepared in situ by bubbling F_2 into out-of-specification NT0 containing 0.22 weight percent water equivalent. This method of preparing INTO was found to be unfeasible, however, because of the excessive time required for sufficient fluorine to react. INTO was found not to be storable in the large tanks after it had been made in situ. It was not established whether this was due to the surfaces having been badly corroded by the addition of fluorine, to lack of sufficient passivation, or simply to a general lack of storability.

Stress corrosion tests with titanium 6Al-4V in INTO at 70 C or ambient resulted in no specimen failures and no indication of excessive chemical attack.

Small-bomb storability tests were conducted with two INTO samples prepared from NT0 containing 0.08 and 0.2 weight percent water, respectively. The alloys tested were 250 maraging steel, A286 steel welded with Hastelloy-W rod, and titanium 6Al-4V. INTO was found to be storable in A286 steel (14 months, ambient and 70 C) but not in 250 maraging steel or titanium 6Al-4V. Short-term storability tests were also conducted at 130 C.

It was not expected that the small amount of FNO_2 in INTO would produce an unstable or sensitive mixture. The anticipated insensitivity of INTO has been verified experimentally.

Methods were developed for the determination of trace amounts of Cr, Cu, Al, Ni, Fe, and Ti in both NTO and INTO. A hydrolysis technique followed by atomic absorption spectrometric analysis was found to offer a simple, rapid, and specific method for the determination of trace metals. Enhancement of the sensitivity for metals was obtained by using methods involving four-fold and twenty-fold concentration by evaporation.

The long-term (21 month) corrosion and storability tests (AFRPL-TR-66-320) were completed. The generally held presumption that "wet" NTO (>0.1 -percent water equivalent) is highly corrosive was conclusively disproven in these long-term coupon corrosion tests which included tests with NTO containing 0.33 weight percent water. It was found that the corrosion rate dropped off drastically after a short period of exposure; it was for this reason that the previous short-term tests with wet NTO had given incorrect (extrapolated) corrosion rates.

Several of the metals studied seem to passivate well against attack by the FNO_2 and HF in INTO. This suggests that practical passivation techniques could have been developed for this oxidizer system had the long-term results verified the general presumption that wet NTO is a highly corrosive liquid with most metals.

Additional small-bomb storability tests at ambient (25 months), 70 C (25 months), and 130 C (49 hours) indicated that INTO is storable and may be used with 304L stainless steel, 321 stainless steel, 6061 aluminum, and nickel when the containers are sufficiently passivated.

Stress corrosion tests were also run with the two current propellant-grade NTO's defined by MIL-P-26539 and MSC-PPD-2A, respectively. Neither oxidizer caused stress corrosion under the test conditions employed (ambient, notched specimens, 45 days) but test specimens of two of the alloys tested underwent a reduction in ultimate strength when contacted with MIL-P-26539 NTO.

INTRODUCTION

Data available at the start of the programs described herein indicated that the use of nitrogen tetroxide (NTO) would be seriously hampered by corrosion problems (Ref. 1, 2, 3, and 4). The references listed asserted that dry NTO would not be a highly corrosive liquid, but that moist NTO would be extremely corrosive, perhaps because of the formation of nitric and nitrous acids by the reaction of NTO with water.

It had previously been demonstrated under Contract AF 04(611)-10809 (Ref. 5) that the addition of a fluorine oxidizer to NTO leads to a reduction of the nitric and nitrous acid content of the propellant with the concurrent production of HF. It had also been shown (Ref. 5) that if the fluorine oxidizer is FNO_2 , the resulting oxidizer system is storable at 70 C in passivated aluminum, stainless-steel, and nickel containers. The NTO- FNO_2 mixtures containing 1 to 3 weight percent FNO_2 were designated inhibited nitrogen tetroxide* or INTO. This report summarizes all of the work performed at Rocketdyne since the issuance of Ref. 5 on the development of INTO.

This report is divided into three separate sections because the work was performed under three contracts: AF 04(611)-10809, F04611-67-C-0008, and F04611-67-C-0099. For convenience, the reports for the three programs have been combined into a single document. Some of the initial work on INTO reported in Ref. 5 is not repeated in this report.

*Subsequently, NTO inhibited by the addition of NO, MSC-PPD-2A, has been designated by NASA as "inhibited nitrogen tetroxide."

RESEARCH ON INHIBITED N_2O_4 , CONTRACT F04611-67-C-0008

TASK I: LARGE-TANK STORAGE

INTRODUCTION

The objectives of this task were to investigate the storability of inhibited NTO (INTO) in large tanks (greater than approximately 10-gallon capacity), and to investigate the in situ formation of $FN O_2$ (the inhibiting agent) using out-of-specification NTO. The original plan was to store six tanks, each fabricated of a different alloy, for a period of 12 months at ambient temperature. In addition, six identical tanks were to be stored at 70 C for the same period. Of the 12 tanks, 10 were loaded with NTO and INTO was produced in situ by fluorine addition. These 10 tanks were stored under the required test conditions until all the $FN O_2$ was exhausted. The remaining two tanks, both titanium, failed during the process of fluorine addition.

EXPERIMENTAL

Materials

Two tanks of the capacity listed were constructed of the following alloys:

- Type 347 stainless steel, 18 gallon
- Type 1018 carbon steel, 10 gallon
- 18 percent nickel-maraging steel, 10 gallon
- Type 2219 aluminum, 10 gallon
- Type 2014 aluminum, 10 gallon
- Titanium 6Al-4V, 24 gallon

All NTO came from a single 2000-pound cylinder. The NTO used was out of specification and contained 0.22 weight percent water equivalent by phase separation analysis.

NTO Loading

The NTO loading was accomplished by gravity flow. The total amount of NTO added was controlled by weighing the tanks when empty and during the fill operation.

Fluorine Addition

After the NTO addition had been completed, F_2 was bubbled into the tanks through perforated dip legs. The tanks and the NTO and fluorine loading systems are shown in Fig. 1.

During the day, the tank ullage pressures were increased approximately 70 psi by fluorine addition. After standing overnight, an ullage pressure drop was noted, presumably due to FNO_2 dissolution. In the morning, the tanks were vented until a constant vapor pressure was observed (no decrease in ullage pressure upon further venting). The 8 tanks of 10-gallon capacity were loaded simultaneously from a common manifold; 27 pounds of fluorine were added over an 18-day period.

The in situ formation of FNO_2 by the addition of fluorine was slower and more difficult than had been anticipated. This is shown by the following description of the loading of the two 347 stainless-steel tanks.

The two tanks, No. 1-A and 2-T, were filled with 168 and 162 pounds of wet NTO, respectively. Fluorine was bubbled through the tanks at an average rate of 0.07 lb/hr. This slow rate ensures the formation of FNO_2 , whereas rapid fluorine addition might result in the formation of some FNO . The reaction leading to FNO_2 formation ($N_2O_4 + F_2 \rightarrow 2FNO_2$) was well controlled in the loading operation with no pressure or temperature surges being detected.

Fluorine was injected into the tanks at pressures up to 100 psi instead of the anticipated 50 psi. This 100-psi loading pressure was necessary because of higher than expected tank ullage pressures. Tables 1 and 2 show data from the logbook for the loading of tank 1-A, and illustrate

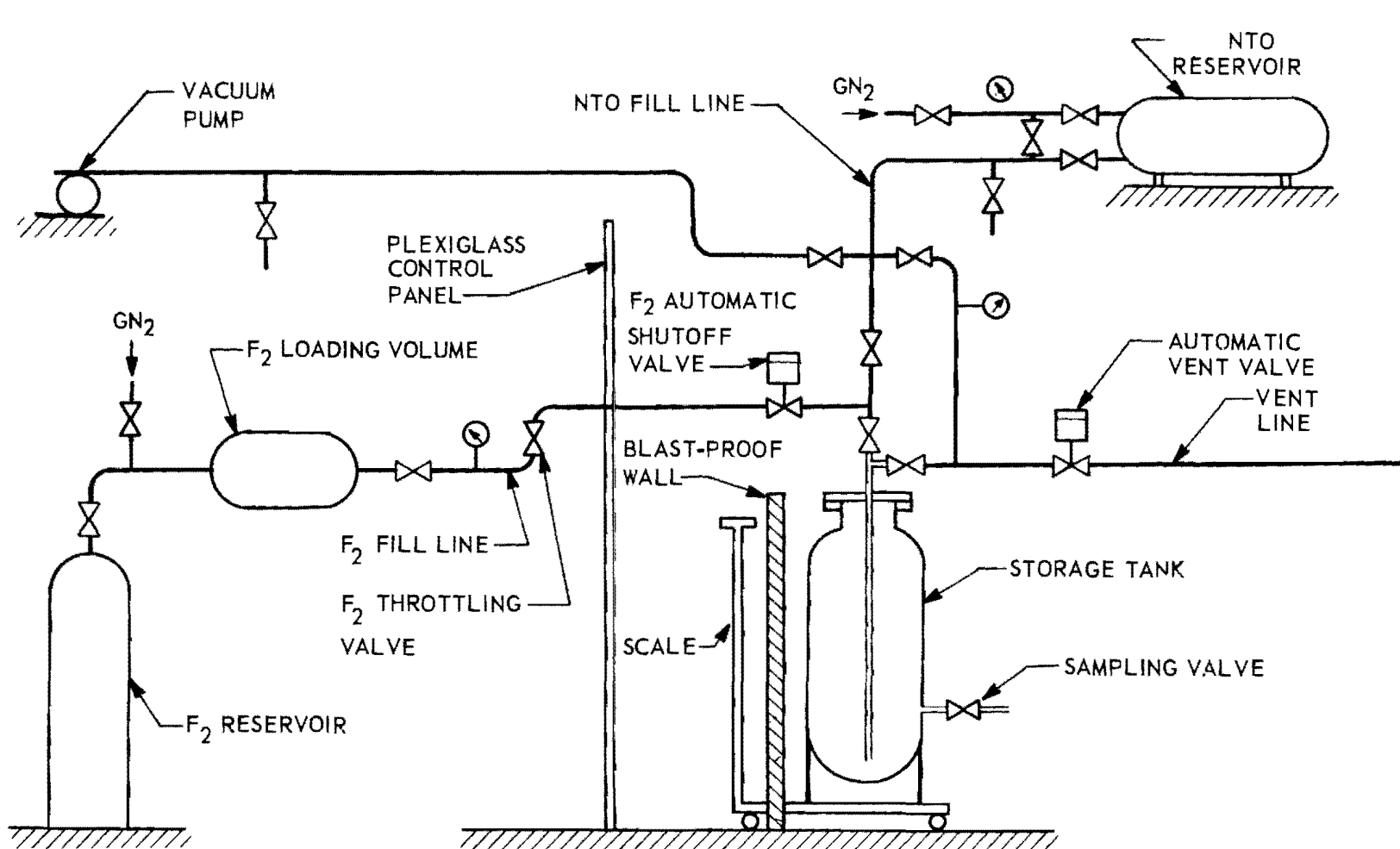


Figure 1. Loading Facility Schematic

TABLE 1

TANK 1-A DATA SHEET

Date, 1967	F ₂ Loading Volume Pressure, psig	Tank Ullage Pressure, psig	Remarks
2-7	50	7.5	
	35	25	Tank ullage vented
	49	10	
	35.5	28.5	Tank vented to 10 psig
2-8	58	5	
	44.5	40	Tank ullage vented
	65	15	
	55	50	Tank ullage vented
	78	21.5	
	65	60	Tank ullage vented
	85	30	
2-9	73.5	65	
	80	27.5	Ullage dropped 28 psig overnight (vented to 27.5)
2-13	73.5	50	
	72	0	Tank ullage vented
	50	45	
2-14	79	11	Ullage dropped 18 psig overnight (vented to 11)
	60	54	
2-15	84	14	Ullage dropped 15 psig overnight (vented to 14)
	61	57.5	
2-16	84	20	Ullage dropped 12.5 psig overnight (vented to 20)
	67	63	Tank ullage vented
	84	20	
	70	66	
2-17	90	18	Ullage dropped 15 psig overnight (vented to 18)
	72	70	
2-20	95	19	Ullage dropped 20 psig over week- end (vented to 19)
	70	67	
2-21	--	61	Ullage vented and tank stored
	--	36	

TABLE 2

TANK 1-A FLUORINE MASS BALANCE

	<u>Weight, pounds</u>
NT0 Loaded	168
Total H ₂ O Equivalent in NT0	0.37
F ₂ Required to React H ₂ O	0.78
FN0 ₂ Concentration (4.4 mole percent)	
F ₂ as FN0 ₂	1.52
F ₂ Reacted	0.78 + 1.52 = 2.30
F ₂ Added	2.65
F ₂ Balance (vented or passivated out)	0.35

the ullage pressure history. For the FNO_2 concentrations in question, the vapor pressure of the INTO should range between 15 and 25 psig (Ref. 5). As Table 1 shows, ullage pressures have been as high as 70 psig. Two reasons have been postulated for this high pressure: (1) an FNO_2 -nitric and nitrous acid reaction resulting in gaseous oxygen evolution, and (2) a slow rate of dissolution of FNO_2 into the bulk liquid.

The mass balance in Table 2 shows that the formation of FNO_2 is nearly quantitative. Only one-seventh of the fluorine added contributes to venting losses and tank passivation. Additional passivation will probably take place during storage. The remarks in Table 1 show that the tank ullage pressure decreases 12.5 to 28 psi overnight. Temperature drop overnight could account for no more than 5 psi of this decrease. It was noted during the loading of tank 2-T that the higher the ullage pressure, the greater the pressure drop overnight. It appears that equilibrium of FNO_2 between the vapor phase and the solution is being established slowly, thus the second postulate of slow dissolution of FNO_2 is favored.

Facility Buildup

Because of the toxic and explosive properties of the propellants involved, a special facility was built up at Rocketdyne's Santa Susana Field Laboratory to perform the above operations. A floor plan of the facility is presented in Fig. 2.

Infrared Analysis

The contents of the tanks were analyzed for FNO_2 content by infrared spectrophotometry. The portable sampling rack built for this purpose is shown schematically in Fig. 3. The sampling operation was performed as follows:

1. The sampling system (which had been prepassivated with FNO_2) was evacuated.
2. A liquid sample was trapped between the tank sampling valve and the expansion valve.

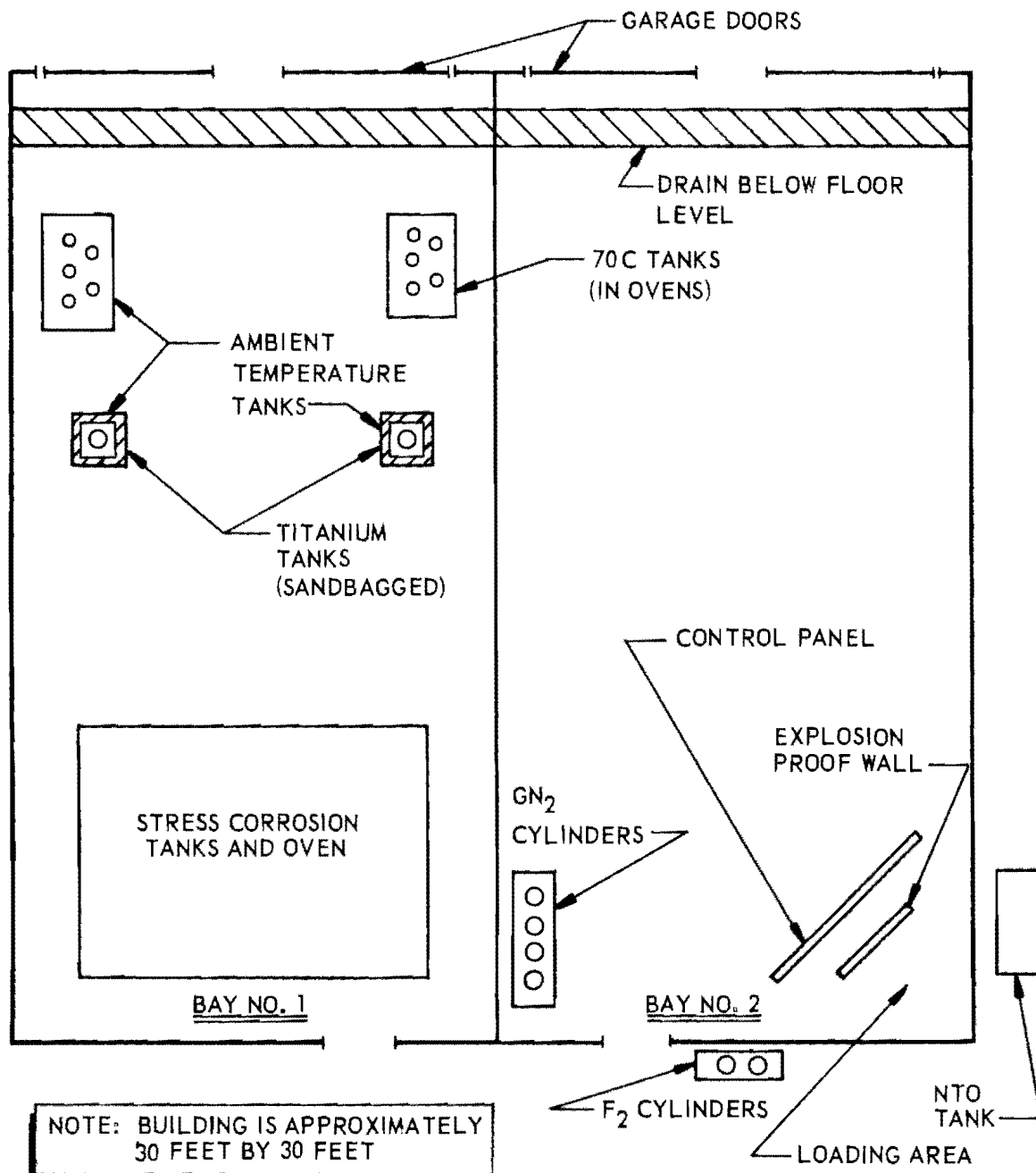


Figure 2. Floor Plan of INTO Facility

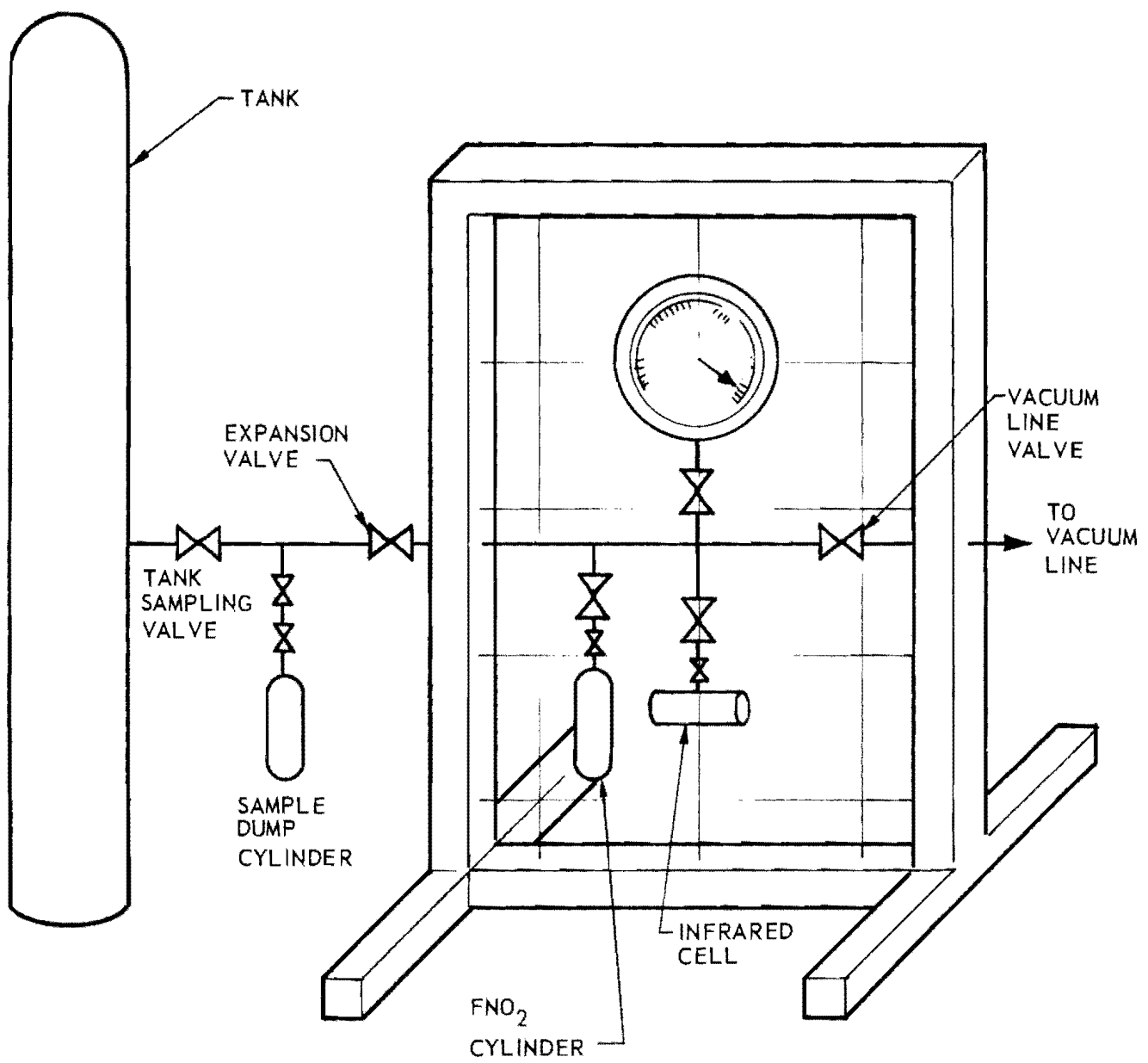


Figure 3. Portable Sampling Rack Schematic

3. The sample was expanded into the infrared cell until the desired pressure was reached.
4. Excess liquid sample was transferred to the sample dump cylinder.
5. The gas sample was then analyzed on an infrared spectrometer.

RESULTS AND DISCUSSION

All of the tanks were successfully filled with INTO. Fluorine addition was also successful, although much slower than anticipated, with all but the titanium tanks. The titanium tanks failed towards the end of the fluorine addition procedure, spilling 20 to 30 pounds of INTO onto the concrete floor of the test facility. Safety procedures previously set up for such a contingency resulted in immediate detection and subsequent correction with minimum damage to equipment.

The titanium tanks were spherical and were mounted on square aluminum frames, thus being supported at four points of contact. Each tank failure occurred at a contact point where the weight of the tank was concentrated. Close visual examination of the tanks revealed that severe corrosion had occurred over the interior surface. The corrosion was more severe where the fluorine had been introduced. There was evidence that the corrosion occurred at an accelerated rate (stress accelerated corrosion) at all of the load bearing points. The photograph (Fig. 4) appears to reveal corrosion of the outer surface, but the apparent corrosion was caused by corrosion products from the interior of the tank being washed onto the exterior surface and drying there. A water rinse completely removed the apparent corrosion. As a result of the tank failures and of the small-bomb storability tests with titanium 6Al-4V, reported later, it was concluded that INTO is not storable in this alloy. Table 3 gives the results of infrared analysis for FNO_2 on the tanks which were successfully charged with INTO. The FNO_2 content of all tanks, except the 1018 carbon steel tank stored at ambient temperature, dropped rapidly with time--the rate being much faster at 70 C. Additional fluorine was charged



Figure 4. Photograph of Titanium 6Al-4V Tank After Failure

TABLE 3

LARGE TANK STORAGE DATA

Material	Temperature	Weight Percent FNO_2 After Indicated Months of Storage					
		0	1	2	3	4	5
347 SS	Ambient 70 C	3	1	$(2)^a$		0	
		2	0				
1018 Carbon Steel	Ambient 70 C	5	5	$(3)^a$	4	0	
		3	0				
250 Maraging Steel	Ambient 70 C	4	4	$(4)^a$		0	1
		4	0				
2014 Aluminum	Ambient 70 C	4	3	$(3)^a$		0	1
		4	0				
2219 Aluminum	Ambient 70 C	3	2	0			1
		1					

^aRecharged by removing from test and bubbling in more fluorine

into four of the tanks from the 70 C test to determine if only initial passivation was involved. These again depleted rapidly, and the large tank storage tests were terminated because of the negative results obtained.

These data definitely show that INTO is not storable in these tanks at 70 C. Some drop off in FNO_2 content was expected as the tanks passivated but the extent of reaction encountered exceeded the limits of mere passivation. Whether this lack of storability would also have occurred if the tanks had been prepassivated is uncertain; small containers of similarly based alloys (321SS and 6061 aluminum) had not reacted with FNO_2 after prepassivation with F_3NO and ClF_3 gases (Ref. 5).

CONCLUSIONS

The production of INTO in situ by bubbling F_2 into NTO has been accomplished but appears to be impractical because of the excessive time required for sufficient fluorine to be added. The pressure rises in the system were high per mole of F_2 added. This could be due to any of the following four causes or to combinations thereof:

1. Heating of the solution due to the chemical reaction.
2. Unreacted F_2 remaining in the gas phase for several hours.
3. Slow dissolution of FNO_2 .
4. The production of volatile byproducts; e.g., O_2 by the reaction



No indication of solution heating was observed and other reactions run in this laboratory between F_2 and N_2O_4 have been quickly completed. Hence, the high pressure rises observed were most probably primarily due to causes 3 and 4.

INTO was not found to be storable in the large tanks after it had been made in situ. Whether this was due to the surfaces having been badly corroded by the F_2 addition, to lack of sufficient passivation, or simply to a general lack of storability is uncertain. On the basis of these studies, it must be concluded that INTO is not storable in the above materials when prepared in situ from out-of-specification NT0.

TASK II: TITANIUM STRESS CORROSION,
CONTRACT F04611-67-C-0008

INTRODUCTION

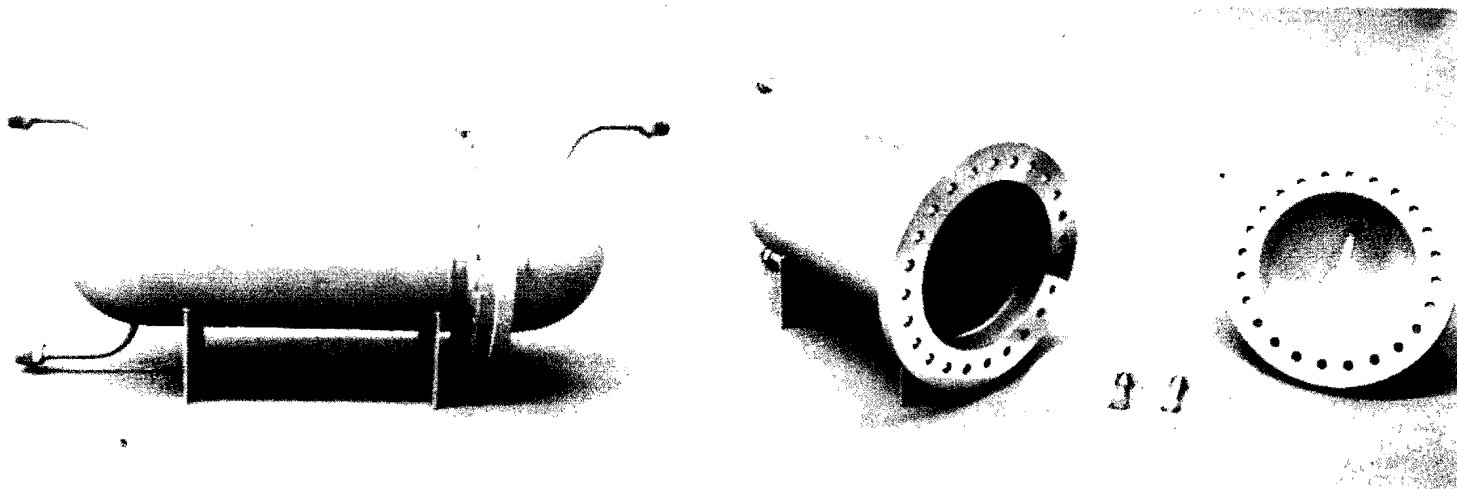
Stress corrosion problems have been encountered with titanium alloys in contact with NT0 propellant. It has not been definitely established which chemical moieties in the propellant participate in this process. Because the addition of FNO_2 to NT0 will affect the chemical species which are present, a study of titanium stress corrosion was conducted in the presence of INT0.

EXPERIMENTAL

Tanks

Two tanks were constructed to hold the INT0. The design is shown in Fig. 5. The material was 6Al-4V titanium alloy throughout, except for the flare fittings which were stainless steel, the bolts (A286 alloy), and the Teflon gasket. The inside diameter was 6-1/4 inches with hemispherical ends, and a 10-inch straight section between these. Fill, sampling, and vent tubes were installed as shown in Fig. 5B. Wall thickness was 0.63 inch.

The tanks were pressurized hydrostatically to 270 psig, maintained for 2 minutes at that pressure, and depressurized. This procedure was repeated five times. There was no leakage. The tanks were fabricated by TIG welding in a chamber containing an argon-helium atmosphere and were radiographically inspected to Rocketdyne Class I requirements (RA 0611-006). After welding, the parts were stress relieved for 3 hours at 538 C, finish machined, and chemically cleaned.



A: Titanium tank for stress corrosion testing. Fill tube is at right, sampling at lower left, and vent at upper left. Tank was entirely titanium, except for the Teflon gasket, A286 bolts, and stainless-steel flare fittings.

B: Titanium stress corrosion test tank, disassembled. Bolts were tightened to 30 lb-ft torque. No leakage occurred.

Figure 5. Stress Corrosion Testing Tanks

Stress Corrosion Frames

The stress corrosion frames are shown in Fig. 6. They were made entirely of 6Al-4V titanium alloy. The frames were rough machined and then heat treated as follows;

1. Degreased in acetone
2. Solution treated in air at 954 C for 1 hour, then water quenched for 4 seconds maximum.
3. Aged in air at 538 C for 8 hours, then air cooled

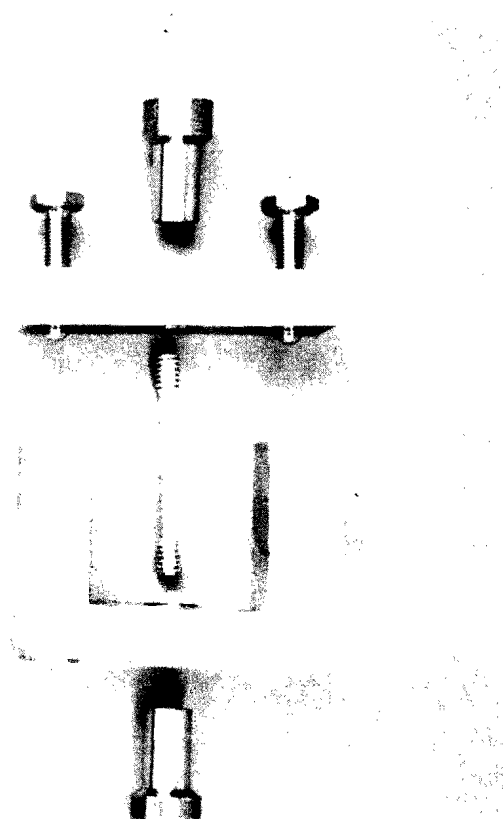
The frames were then finish machined, removing all surface contamination from the air, and then cleaned and packaged.

Specimen Stressing

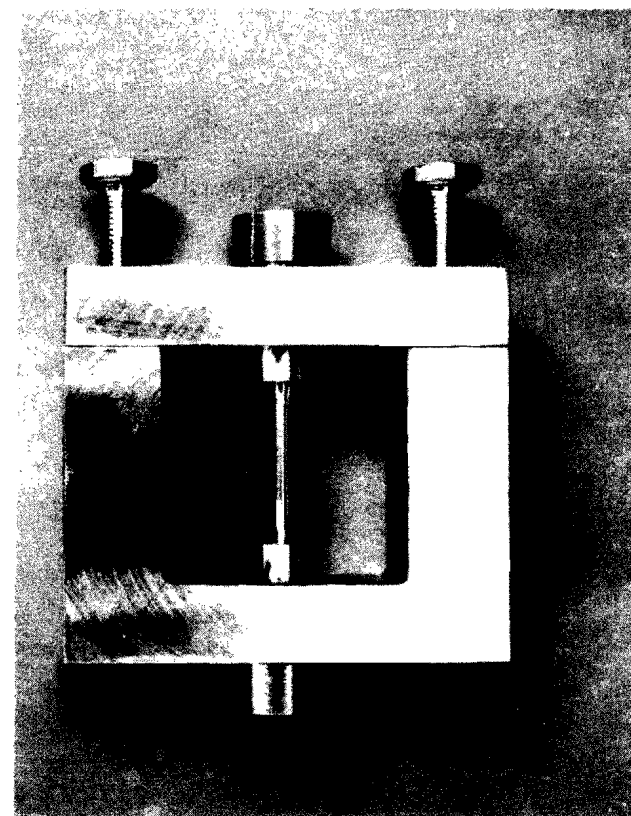
The specimens were to be loaded to 90,000 psi in tension during the test. Three specimens were selected at random. Each was stressed to 90,000 psi in a tensile machine and the extension under load recorded on a chart. This test was repeated three times for each specimen. From the nine tests, an average stress-strain slope of 12.2×10^6 psi and an average extension of 0.00523 in./in. were determined. Using the same extensometer, the specimens were loaded in the stress frames by torquing the cap screws to produce the required extension (Fig. 6).

Tank Loading

The loaded frames were cleaned in acetone and loaded into racks in groups of three, as shown in Fig. 7A. Two racks were loaded into each tank. These racks were positioned in the tanks at different heights supported on rails as shown in Fig. 7B. The volume of liquid to be added was calculated to provide for complete immersion of one set of three and to position the liquid-gas interface in the middle of the specimens in the other set. After positioning the frames in the tank, the gasket was inserted and the bolts tightened uniformly to 30 lb-ft torque.

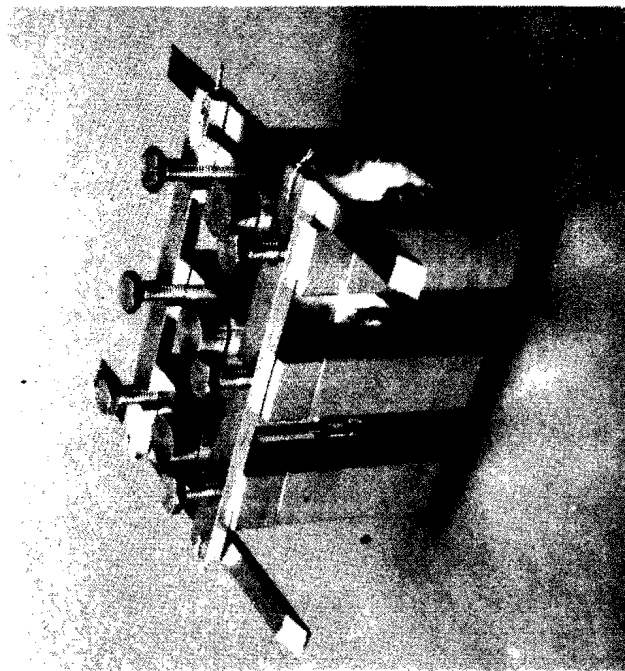


A

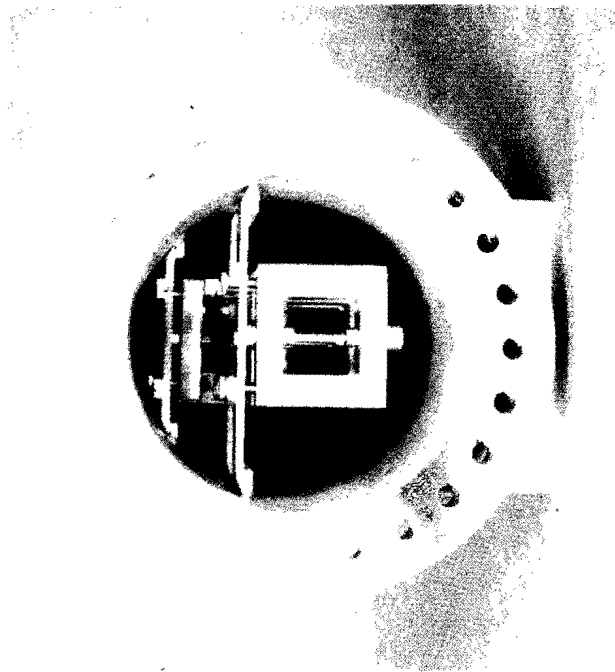


B

Figure 6. Titanium Stress-Corrosion Test Frames. (Specimen is threaded into the end nuts, which in turn fit into the frames. Stress is applied by tightening the cap-screws. Spherical-ends of the cap screws mate into spherical seats in the frame proper.)



A



B

Figure 7. Loading and Supporting of Stress Frames in Tanks

Three frames, with their stress specimens, were stored in a dessicator as controls. Other specimens were maintained unstressed at room temperature.

Specimen Preparation

The raw material was purchased from Titanium Metals Corporation of America as 1.0-inch bar stock conforming to AMS 4923B, mill annealed. Pertinent information concerning the material, as certified by the vendor, is presented in Tables 4 and 5.

The metallographic structure of the material as received, taken at the center of the 1.0 inch round, is shown in Fig. 8. The structure is well defined alpha-beta, fine grained, and very clean.

The 1.0-inch-diameter stock was abrasively cut into quarters, from which the specimens were to be made. After cutting, the material was heat treated as follows:

1. Cleaned in acetone
2. Vacuum annealed at 760 C for 4 hours, then vacuum cooled to 427 C, and air cooled
3. Solution treated in air at 954 C for 1 hour, then water quenched for 4 seconds maximum
4. Aged in air at 538 C for 8 hours then air cooled

After heat treatment, a metallographic examination confirmed that no contamination had occurred that would not be eliminated during machining. The pieces were then finish-machined.

Inspection for Failures

To determine whether any specimens had failed without opening the tanks, a radiographic technique was developed. An Iridium 192 pill was used, initially approximately 10 curies. By photographing horizontally through the tank with the film set vertically behind it, excellent resolution was

TABLE 4

VENDOR'S CERTIFICATION OF CHEMICAL ANALYSIS
OF TEST BAR MATERIAL (HEAT #G1750)

ELEMENT	AMOUNT, percent
C	0.024
Fe	0.14
N	0.014
Al	6.4
V	4.2
H	0.005
O	0.12

TABLE 5

VENDOR'S CERTIFICATION OF MECHANICAL PROPERTIES
OF TEST BAR MATERIAL (HEAT #G1750)

Yield Strength, psi	138,000
Tensile Strength, psi	143,500
Elongation, percent in 2 inches	20
Reduction of Area, percent	47
Notched time fracture 150,000 psi in 5 hours	
Elevated temperature properties, 1/2 hour at 700 F	
Yield Strength, psi	84,500
Tensile Strength, psi	101,300
Elongation, percent in 2 inches	19
Reduction of Area, percent	57
Beta Transus	1825 F to 1835 F

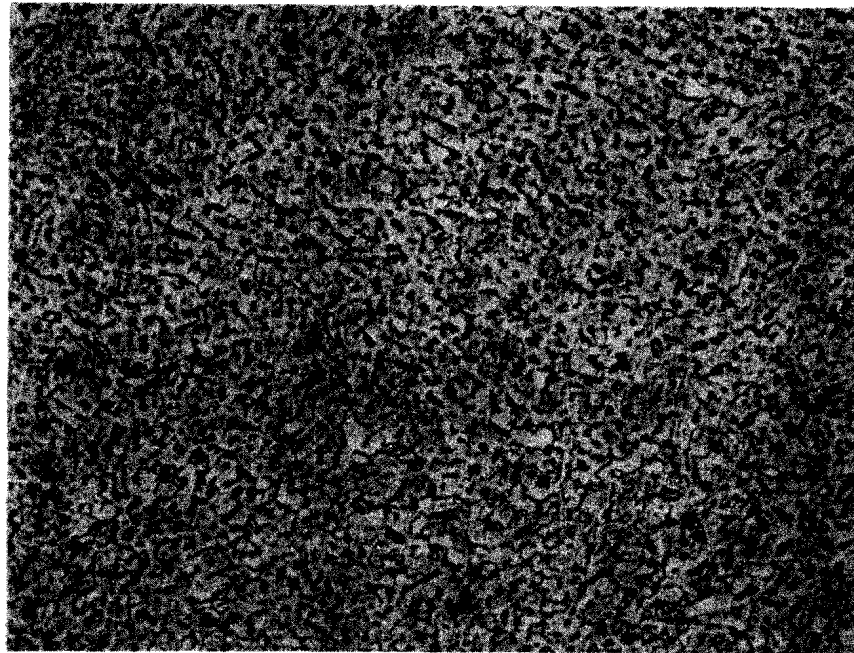


Figure 8. Structure of Specimen Material. (This photomicrograph is a cross-section through the as-received bar, 1.0 inch diameter, taken at the center; well defined alpha-beta, fine grained, and very clean; Keller's etchant; 500X.)

obtained with a 3-minute exposure on Type A film at 3 feet. The lower portion of the frame is held in position by the specimen (Fig. 6A). In the event of failure, the frame would drop to the bottom of the tank, and this would be immediately evident on the radiograph.

RESULTS AND DISCUSSION

The contents of the tanks were sampled to determine their FNO_2 contents at the start of the test and weekly thereafter. At all times, the FNO_2 concentrations remained above the lower limit of the INTO range. The results of the first and last analysis on both tanks are presented in the following table:

FNO_2 CONTENTS OF STRESS CORROSION TANKS

Tank	Test Temperature	FNO_2 Content, mole percent	
		26 May 1967	20 June 1967
1	70 C	5.8	1.9
2	Ambient	5.7	5.0

The stress corrosion tests were terminated on 6 July 1967 due to penetration of the two titanium 6Al-4V storage tanks reported in Task I. The 70 C tank was removed from the oven, but neither tank was cleared of INTO until 7 July 1967; there was a total of 43 days exposure. After venting out of the tanks, they were purged with dry nitrogen.

On 10 July 1967, the tanks were opened in a dry box. The condition of the interior is shown in Fig. 9. All titanium alloy surfaces were coated uniformly with a cream-colored layer, 0.010 inch thick. This coating was highly hygroscopic, and dissolved on absorbing moisture from the air releasing NO_2 . In Fig. 9 this absorption process has already occurred. After flushing with water, the tank interior appeared smooth and no pitting was evident to the unaided eye. None of the stress corrosion

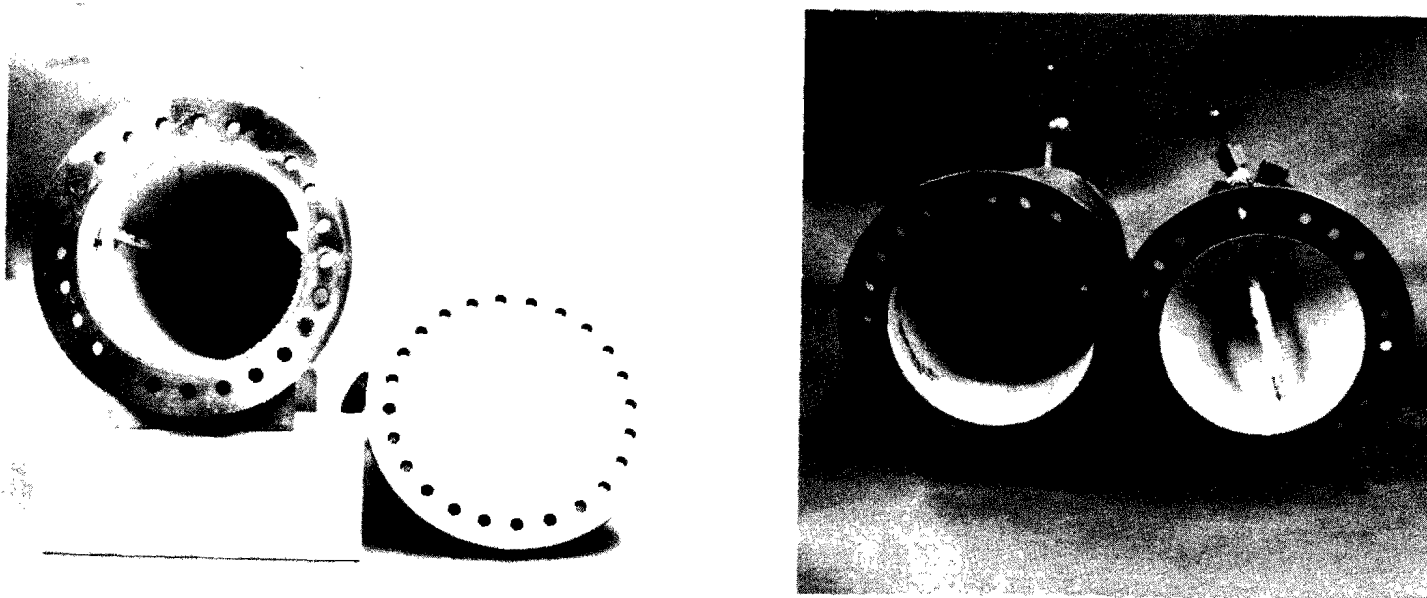


Figure 9. Condition of Tanks Immediately After Opening
(Water absorption from the atmosphere has
already begun.)

specimens had broken. There was no apparent difference in the condition of any of the specimen groups, regardless of exposure situation. All were uniformly coated with the same cream-colored coating. Representative groups in several stages of coating dissolution are shown in Fig. 10. Again, the coating was approximately 0.010 inch thick.

The stress corrosion tanks were not as severely attacked by the preformed INTO as were the 24-gallon titanium tanks by INTO prepared by adding out-of-specification NT0 and then bubbling in fluorine to form the INTO in situ. However, results on small bombs obtained during Task III indicate that titanium 6Al-4V will not passivate against even preformed INTO. Thus, the lesser attack noted in the stress corrosion tanks indicates only that the reaction was slower.

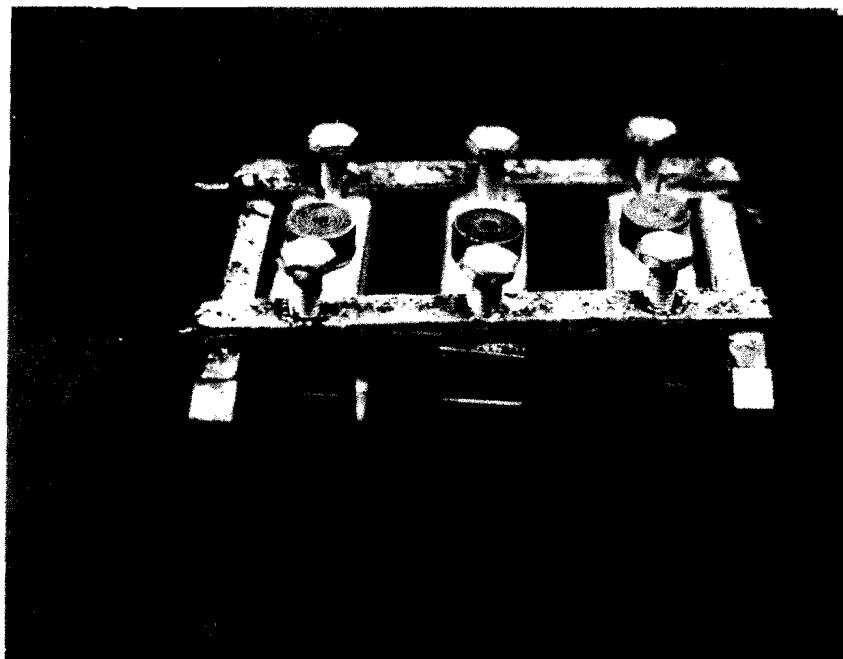
Measurements of specimen diameter after rinsing off the coating indicated that between 0.005 and 0.001 inch of metal had been removed. The specimens were fitted with the same extensometer used in loading, and the load was released. All specimens contracted slightly more than they had originally been stretched, due to cross-sectional decrease by corrosion. The results of tensile tests on the 12 specimens are presented in Table 6. Results on six identical control specimens stored unloaded in air are presented in Table 7. It is evident that there was no significant deterioration of the specimens due to exposure to INTO during this series of tests. This is corroborated by Fig. 11, which shows a completely normal cup-and-cone ductile fracture, with no indication of embrittlement. Figure 12, at higher magnification, shows the typical alpha-beta structure of 6Al-4V alloy with no indication of localized chemical attack.

CONCLUSIONS

No stress corrosion or indication of excessive chemical attack is observed when stressed titanium 6Al-4V is exposed at 70 C or ambient temperature to NT0 inhibited with FNO_2 for a period of 43 days.

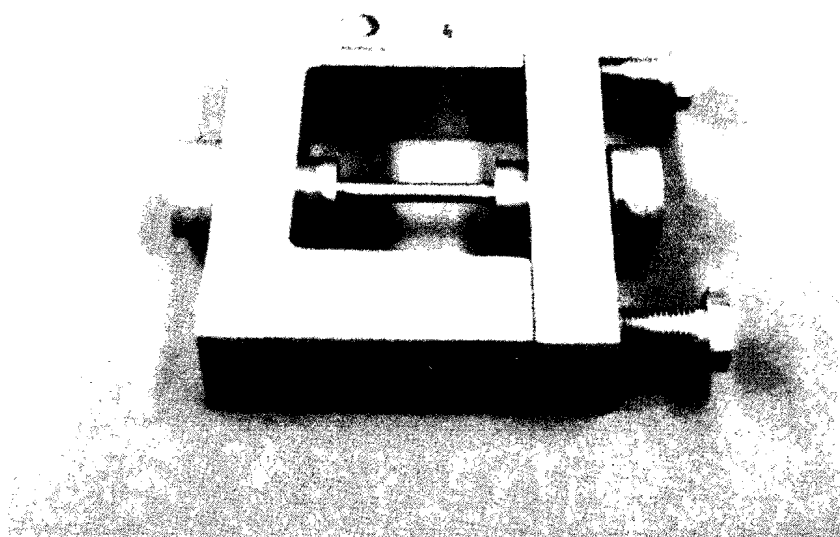


A. Immediately After Removal

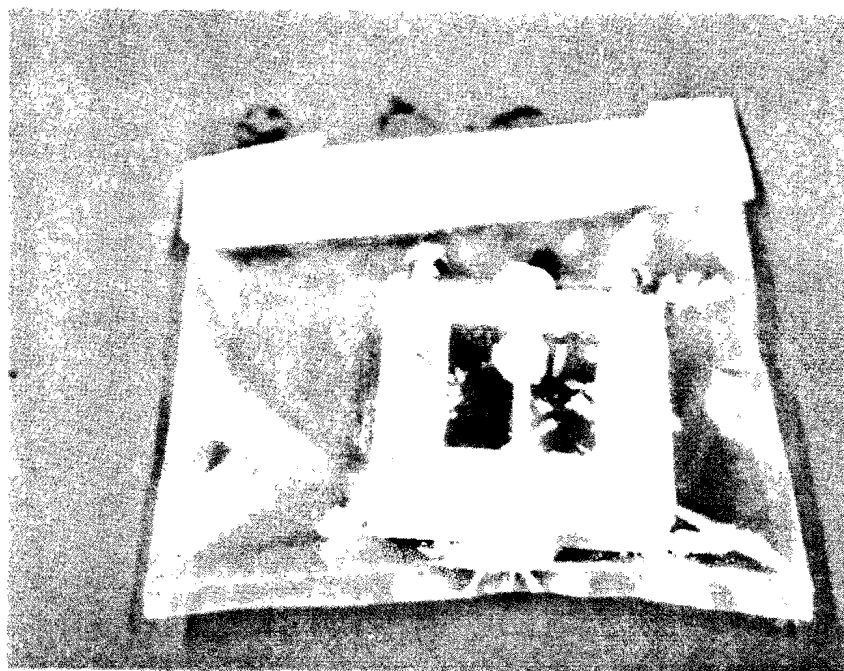


B. After 5 Minutes in Air

Figure 10. Frames and Specimens After Test



C. After Water Rinsing



D. Packaged Before Removal From Dry Box
to Exclude Air

Figure 10.(Concluded)

TABLE 6

MECHANICAL PROPERTY TESTS ON SPECIMENS AFTER EXPOSURE

Specimen No.*	Cross-Sectional Area, sq in.	Yield Strength (0.2 percent offset), psi	Ultimate Strength, psi	Elongation percent in 0.5 inch (0.5 inch = 4 diameters)
101	0.0121	157,800	171,000	16.0
102	0.0119	159,400	175,200	16.0
103	0.0117	159,200	176,000	14.0
Average		158,800	174,700	15.3
111	0.0117	166,800	179,200	14.0
112	0.0119	161,200	176,000	14.0
113	0.0119	161,000	174,000	14.0
Average		163,000	176,400	14.0
201	0.0125	156,000	172,500	14.0
202	0.0121	161,200	174,000	16.0
203	0.0121	160,700	177,000	16.0
Average		159,300	174,500	15.3
211	0.0119	160,000	179,400	14.0
212	0.0123	158,600	173,500	16.0
213	0.0121	161,000	174,000	14.0
Average		159,900	175,600	14.7

*First digit indicates exposure Temperature 1 = 70 C
2 = Room temperature

Second digit indicates exposure type 0 = Half immersed
1 = Fully immersed

Third digit indicates individual specimen

TABLE 7

MECHANICAL PROPERTIES OF CONTROL SPECIMENS

Specimen No.	Cross-Sectional Area, sq in.	Yield Strength (0.2 percent offset), psi	Ultimate Strength, psi	Elongation percent in 0.5 inch (0.5 inch = 4 diameters)
1	0.0121	159,800	176,200	14.0
2	0.0121	159,400	175,700	13.0
3	0.0125	160,300	176,300	14.0
4	0.0125	160,300	176,300	15.5
5	0.0121	157,300	175,200	16.0
6	0.0123	161,300	174,400	15.5
Average		159,700	175,700	14.7

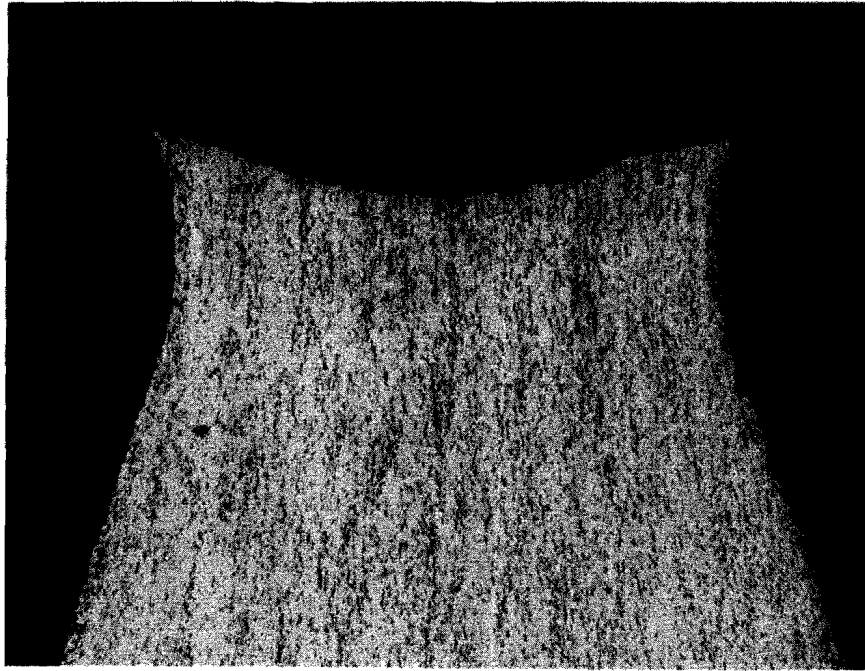


Figure 11. Specimen After Test at 50X Magnification
(Structure is normal and ductile. No
evidence of corrosion is present.)

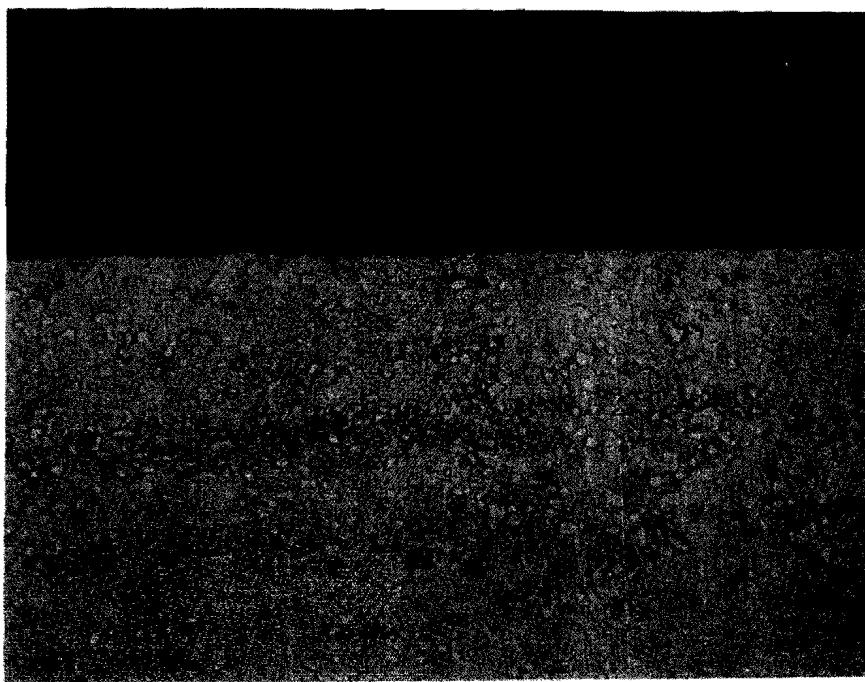


Figure 12. Specimen After Test at 200X Magnification
(No evidence of localized chemical attack.)

TASK III: SMALL-BOMB STORABILITY,
CONTRACT F04611-67-C-0008

INTRODUCTION

Small-bomb storability tests were conducted with two samples of INT0, one prepared from NT0 containing 0.08 weight percent H_2O and the other from NT0 containing 0.2 weight percent H_2O . The bombs (20-milliliter volume) were fabricated of three materials: type 250 (18-percent Ni) maraging steel, type A286 steel welded with Hastelloy-W rod, and titanium 6Al-4V. The tests in containers of 250 maraging steel and of A268 steel were run for 14 months. The tests in titanium 6Al-4V were concluded after 7 months when it became obvious that INT0 was not storable in that alloy. Storage tests at 130 C for 24 hours were also completed.

EXPERIMENTAL

The system used to load the bombs is illustrated in Fig. 13. The bombs were attached to the system at AN fitting No. 3 with all valves shut. Valve No. 2 was opened to the vacuum line and valves No. 3 through 5 were also opened. The system was then pumped until a vacuum was attained between valve No. 1 and the end cap. The vacuum pump was isolated from the vacuum system, the loading assembly was allowed to stand for 30 minutes, and the Heise gage was observed to determine if there was any leakage. Valves No. 2, 3, and 5 were shut off. Valve No. 1 was then opened.

Time was allowed for propellant from the 1-liter Hoke reservoir to fill the 18.5-milliliter volume between valves No. 1 and 3. Valve No. 1 was then closed and valve No. 3 was opened. Time was allowed for the liquid trapped between valves No. 1 and 3 to flow into the storability bomb. Valve No. 4 was then closed. Any excess vapor or liquid still contained between valves No. 1 and 4 was pumped into a -196 C trap on the vacuum line for later disposal. Valve No. 3 was then closed. The storability bomb was disconnected at AN fitting No. 3 and inverted. Valve No. 5 was

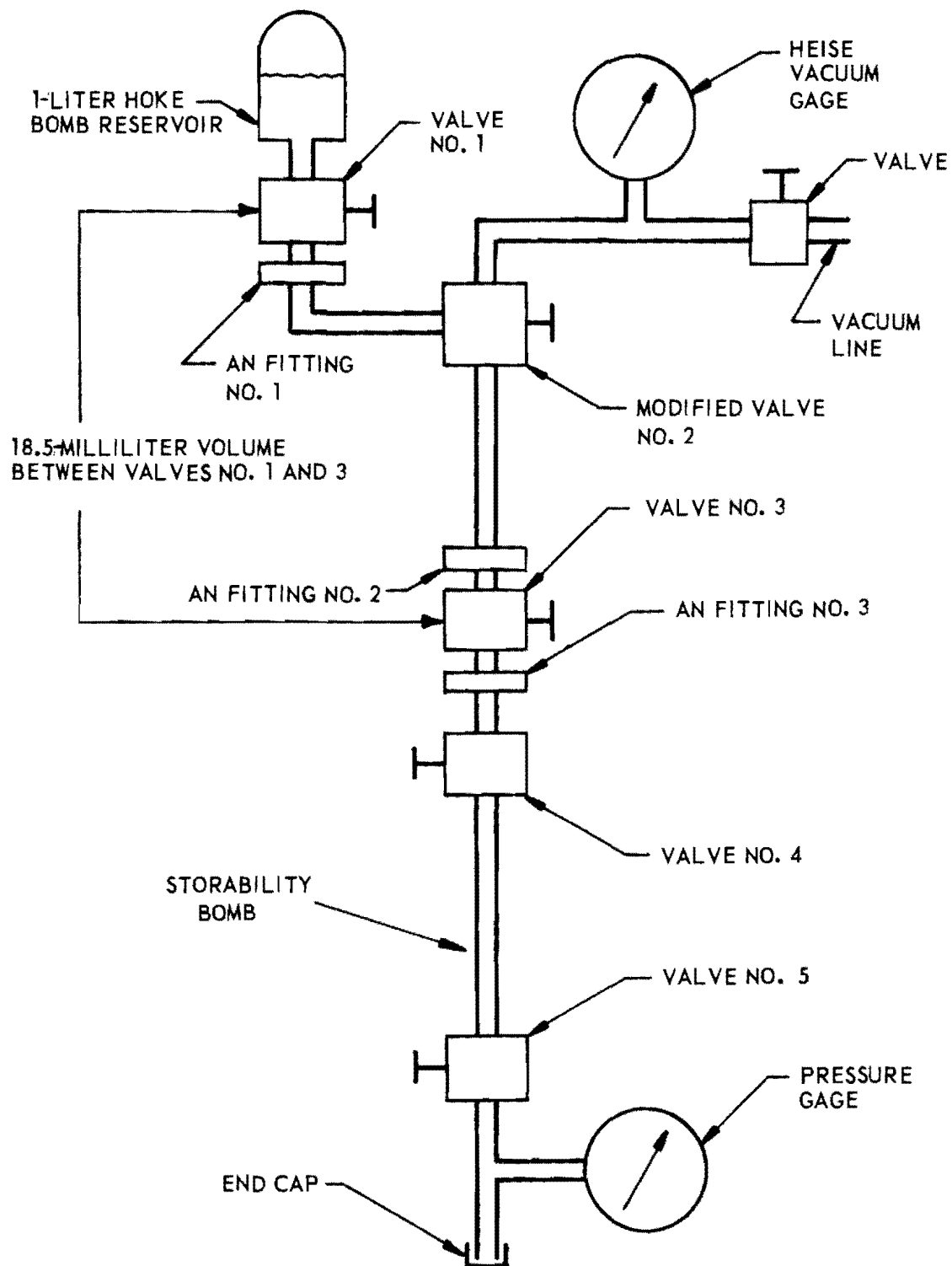


Figure 13. Small-Bomb Loading Assembly

was then opened and the pressure was read. Then valve No. 5 was closed and the bomb was introduced to either an ambient, 70 C, or 130 C temperature environment. The bombs were arranged so that the pressure could be periodically checked by opening valve No. 5. Sampling to determine the composition of the liquid was accomplished through valve No. 4.

RESULTS AND DISCUSSION

The bombs were loaded according to the procedure described above. Analysis for FNO_2 was carried out by expanding a sample of the liquid phase of the INT0 in the bombs to 200-mm Hg pressure in an infrared cell. The concentration of FNO_2 was then calculated from the absorbance at 13.18 microns (NF stretch; Ref. 5). All bombs were passivated for 96 hours at 70 C with a 21 weight percent solution of FNO_2 in NT0 prior to the start of the tests. The results of the 130 C tests are summarized in Table 8.

It may be seen from Table 8 that the FNO_2 contents of the bombs made of 250 maraging steel and of A286 steel welded with Hastelloy W were reduced only approximately 25 to 30 percent during the 24-hour test. However, the FNO_2 was completely consumed in the titanium 6Al-4V bombs during the first 24 hours at 130 C. After the addition of more FNO_2 (equivalent to more extensive passivation), the bombs lost 50 to 75 percent of their FNO_2 in 24 hours at 130 C.

The 70 C and ambient temperature results are presented in Table 9. Examination of Tables 8 and 9 reveals that A286 steel welded with Hastelloy W rod affects the FNO_2 concentration least. At ambient temperature, the FNO_2 content in the A286 test bombs did not change appreciable after 14 months. At 70 C, it only dropped 20 to 30 percent during the first 4 months of testing and then remained essentially constant throughout the next 10 months.

Although much less satisfactory, the 250 maraging steel test bombs exhibited the second best qualities. At ambient temperature, the FNO_2 content dropped

TABLE 8
RESULTS OF 24-HOUR STORAGE TESTS AT 130 C

Bomb Material	Initial Water Content, weight percent	FNO ₂ Content (weight percent) at Various Times, hours			
		0	24	48	76
250 Maraging Steel	0.08*	14*	10	--	--
	0.2**	9**	7	--	--
A286 Steel Welded With Hastelloy W	0.08*	14*	10	--	--
	0.2**	9**	6	--	--
Titanium 6Al-4V	0.08*	14*	0 (11)***	6	3
	0.2**	9**	0 (6)***	2 (6)***	1

*Initial water content of the NTO was 0.08 weight percent; F₂ was added until FNO₂ reached 20.0 mole percent (14 weight percent)

**An additional 0.12 weight percent water was then added to part of the INTO resulting in an initial FNO₂ content of 12.5 mole percent (9 weight percent).

***FNO₂ was added to bring FNO₂ content to that shown in parentheses

TABLE 9

SMALL-SCALE COMPATIBILITY TESTS: 70 C
AND AMBIENT TEMPERATURE DATA

Bomb Material ^a	Initial Water Content, weight percent	Temperature	FNO ₂ Content (weight percent) At Various Times, months				
			0	4	7	10	14
250 Maraging Steel	0.2 ^c	70 C	9	0(13) ^d	9	Trace	0
	0.08 ^b	70 C	14	0(15) ^d	11	0	0
	0.2 ^c	Ambient	9	7	4	0	0
	0.08 ^b	Ambient	14	9	5	Trace	0
A286 Steel Welded With Hastelloy W	0.2 ^c	70 C	9	6	6	6	6
	0.08 ^b	70 C	14	11	9	10	11
	0.2 ^c	Ambient	9	10	11	11	12
	0.08 ^b	Ambient	14	14	13	13	12
Titanium 6Al-4V	0.2 ^c	70 C	9	0(13) ^d	0	--	--
	0.08 ^b	70 C	14	0(15) ^d	0	--	--
	0.2 ^c	Ambient	9	1(13) ^d	10	0	--
	0.08 ^b	Ambient	14	0.5(15) ^d	7	0	--

^aBombs were passivated (with 21 weight percent liquid FNO₂ in N₂O₄) for 24 hours at 70 C prior to test

^bInitial water content of the INT0 was 0.08 weight percent; F₂ was added until FNO₂ reached 20.0 mole percent (14 weight percent)

^cAn additional 0.12 weight percent water was then added to part of the INT0 resulting in an initial FNO₂ content of 12.5 mole percent (9 weight percent)

^dReloaded to this amount

4 to 5 weight percent (absolute) during each 4 months of testing. At 70 C, the FNO_2 was completely depleted after 4 months, and after reloading, it was again completely depleted after 3 more months.

The titanium 6Al-4V tests were least successful. After 4 months at ambient temperature, 90 to 95 percent of the FNO_2 was depleted and, after reloading, 45 to 70 percent of the FNO_2 was depleted after 3 additional months. After 3 more months, the FNO_2 was completely depleted. The apparent slowing of depletion of FNO_2 is not significant because the absolute amount of FNO_2 lost during the period between 4 and 7 months was only slightly less than lost between 0 and 4 months. At 70 C, the FNO_2 content of the titanium 6Al-4V bombs was completely depleted during the first 4 months of testing and, after reloading, the FNO_2 content was again completely depleted after 3 months. The interiors of the titanium 6Al-4V test bombs exhibited considerable pitting when they were opened and washed out with water. The titanium 6Al-4V test bombs were emptied and removed from testing after 7 months because of the failure of the large titanium 6Al-4V tanks discussed in the Large-Tank Storage section of this report and because of the discouraging results with this alloy obtained during this task.

CONCLUSIONS

INTO is storable in A286 steel welded with Hastelloy W, but it is not storable in 250 maraging steel or in titanium 6Al-4V. It is possible that INTO might be storable in these latter two alloys if appropriate passivation techniques were worked out, but such studies were beyond the scope of this investigation.

TASK I: SHOCK SENSITIVITY

INTRODUCTION

It was not expected that the small amounts of FN_2O_2 added to NT_2O to form INT_2O would produce an unstable or sensitive mixture. However, the insensitivity had to be verified experimentally.

The techniques employed to characterize the sensitivity of the FN_2O_2/NT_2O mixtures included the U-tube adiabatic compression test, the detonation propagation test, and the drop weight test.

FN_2O_2 concentrations higher than those of the normal INT_2O range were included in the tests, whenever possible, because concentrated solutions of FN_2O_2 in NT_2O may be used in preparing INT_2O .

U-Tube Adiabatic Compression Test

During this test, a liquid sample is accelerated into the closed end of a steel tube by suddenly applying a driving pressure to the open end of the tube. Extremely high peak pressures and temperatures are generated in the gas bubble trapped between the liquid sample and the closed end of the tube. Sensitive materials will ignite and explode under these conditions, rupturing the tube.

The results of this test are empirical in nature, and the sensitivity of a particular substance must be evaluated by comparing test results with other materials whose handling hazards are well known. The test is a good screening device for discovering substances which may be liable to explosions in feed lines because of sudden valve actuations, etc. A complete description of the apparatus and the theory of its operation is presented in Ref. 6. Test results are usually reported as the pressure ratio (ratio of driving pressure to initial pressure) which yields a

positive result (explosion) 50 percent of the time. As examples of data obtained with standard materials, the 50-percent pressure ratio for ethyl nitrate is 8 if the vapor space contains air, and 24 if it contains only nitrogen (plus ethyl nitrate vapor). Normal propyl nitrate with air has a 50-percent value of 21.

Detonation Propagation Test

Because INTO is volatile, it was necessary to design and build special sealed tubes for the detonation propagation studies.

The test charge is contained in a 1-inch stainless-steel tube. A 0.02-inch stainless-steel sheet is welded onto one end of the sample tube, and a 1/4-inch mild steel witness plate containing a filling valve is welded onto the other end. The 0.02-inch sheet separates the liquid sample from a booster charge of C-4 explosive in a 1-inch tube.

After the booster charge has been set off with a blasting cap, the occurrence or nonoccurrence of a detonation in the test charge is determined through posttest examination of the charge container and the steel witness plate. A negative test results in almost complete recovery of the charge container with no damage to the last few inches and no damage to the witness plate. A positive test results in complete fragmentation and vaporization of the charge container and a hole of approximately the tube diameter completely through the witness plate.

Drop Weight Test

Drop weight tests were conducted using the standard North American Rockwell open-cup impact tester. A small amount of solid material to be tested (e.g., Kel-F) is placed in a 5/8-inch-diameter by 3/8-inch-deep aluminum foil sample cup. The cup is filled with the test fluid and subjected to impact by a falling weight. A control test using water is conducted with each material to determine the posttest condition of the samples due to the impact only.

EXPERIMENTAL

U-Tube Adiabatic Compression Test

The apparatus is described in Ref. 6. Because of the large (approximately 100 cubic centimeter) vapor space above the liquid slug in the U-tube, the liquid composition at equilibrium may be considerably different from the bulk composition loaded into the apparatus. The vapor pressure of FNO_2 is much higher than that of NTO , with the result that most of the FNO_2 remains in the vapor phase. Vapor pressure-composition data for INTO (Ref. 5) were used to calculate the quantities of each component to be loaded into the U-tube to produce a specified final composition in the liquid slug. The apparatus was loaded by condensing each component separately into the U-tube at liquid nitrogen temperature from a known-volume gas-phase loading manifold. For loading purposes, FNO_2 was assumed to be a perfect gas over the pressure range involved (150-to 400-mm Hg absolute). Equilibrium data for the reaction $\text{N}_2\text{O}_4 = 2\text{NO}_2$ as a function of temperature and pressure (Ref. 7) were used to determine the amount of NTO loaded into the system. All tests were conducted at 32 F.

Tests were conducted with compositions of 3 and 7 weight percent FNO_2 in the liquid NTO . Experiments were run with only propellant vapors above the liquid slug and also with 600-mm Hg of air present in the ullage volume. All tests were conducted at the highest driving pressure available (pressure ratio of approximately 100).

Detonation Propagation Test

Figure 14 is a schematic of the test setup which was devised for detonation propagation tests with INTO . The test charge is contained in a 1-inch stainless-steel tube. This tube was welded at one end to a 0.02-inch stainless-steel sheet and at the other end to a 1/4-inch mild steel plate. The 0.02-inch sheet separated the INTO from a booster charge of 50 grams of C-4 explosive in a 1-inch tube. A 1/8-inch stainless-steel valve was screwed into the middle of the 1/4-inch-thick witness plate. This valve was connected to a second valve by a short piece of 3/8-inch tubing.

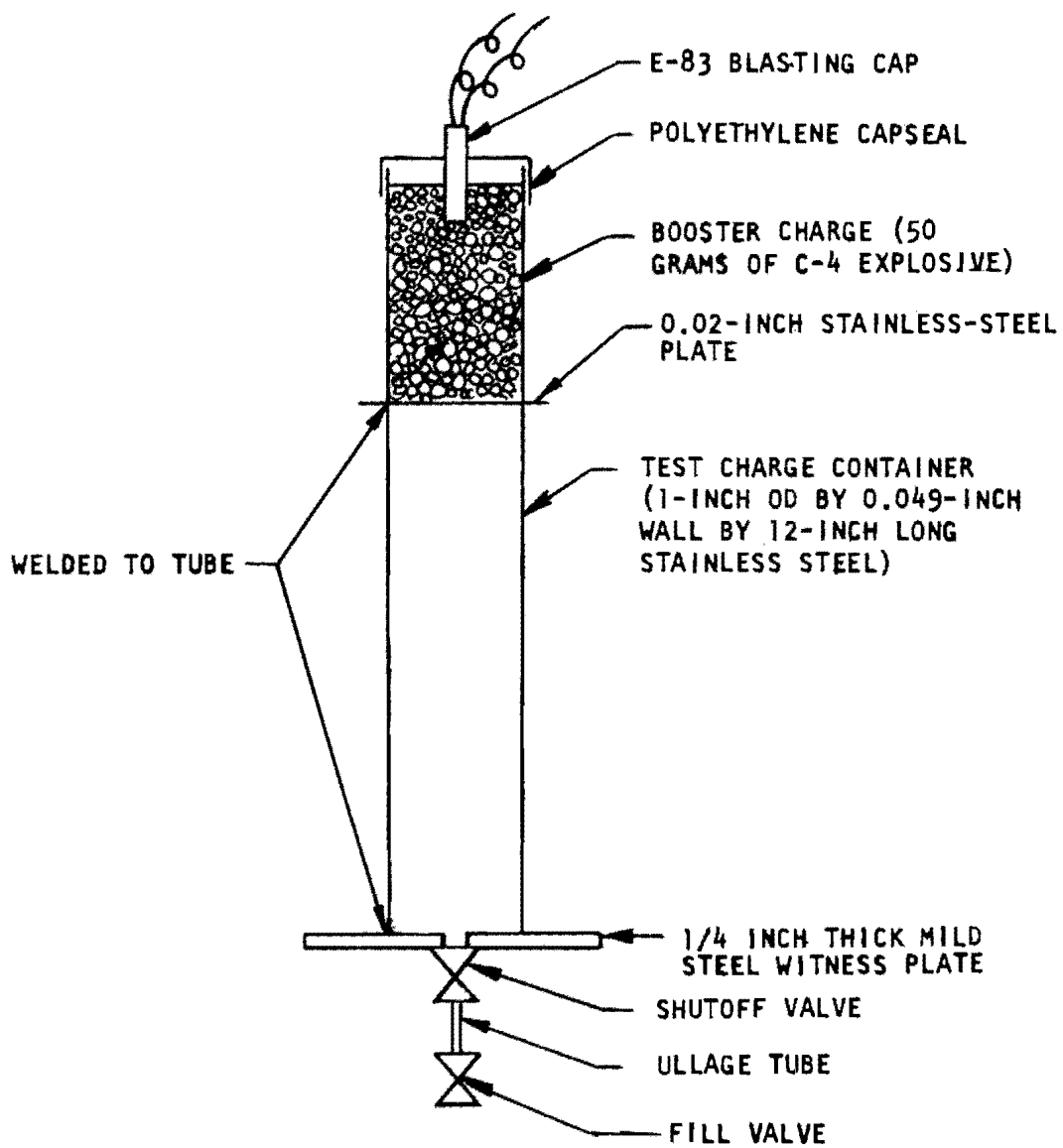


Figure 14. Detonation Propagation Test Setup

To fill the tube for a test, it was inverted and propellant was condensed into the system through the fill valve. The amount of propellant introduced was calculated so that the liquid level was somewhere in the ullage tube. The fill valve was then closed and the charged tube was moved to the detonation test cell. After the explosive charge was attached and all other preparations had been made, the shutoff valve was closed and the tube was inverted so that it was in the position depicted in Fig. 14. The booster charge was then set off with the E-83 blasting cap.

Three tests were conducted with the following test charges: NT0, 3 weight percent FNO_2 in NT0, and 9 weight percent FNO_2 in NT0.

Drop Weight Test

The standard North American Rockwell open-cup impact tester is shown schematically in Fig. 15. A small (approximately 1/10-inch cube) sample of material to be tested is placed in a 5/8-inch-diameter by 3/8-inch-deep aluminum foil sample cup. The cup is then filled with the test fluid and subjected to impact by a falling weight. Filling and impact is carried out as fast as possible to minimize loss of the volatile FNO_2 .

Impact tests were conducted with both 3 and 9 weight percent FNO_2 solutions (analyses were based on pretest composition of the solutions). The following materials were tested: Teflon, Kynar, Kel-F, phenolic resin-cured butyl rubber, Viton-A, and titanium. All tests were performed at the 68 foot-pound impact level. The 3 weight percent FNO_2 solution was tested at ambient temperature. The 9 weight percent FNO_2 solution was precooled to approximately 15 F for reasons discussed below. Five tests were conducted on each material with each propellant. A control test was conducted with each material using water to determine the posttest condition of the samples due to the impact only.

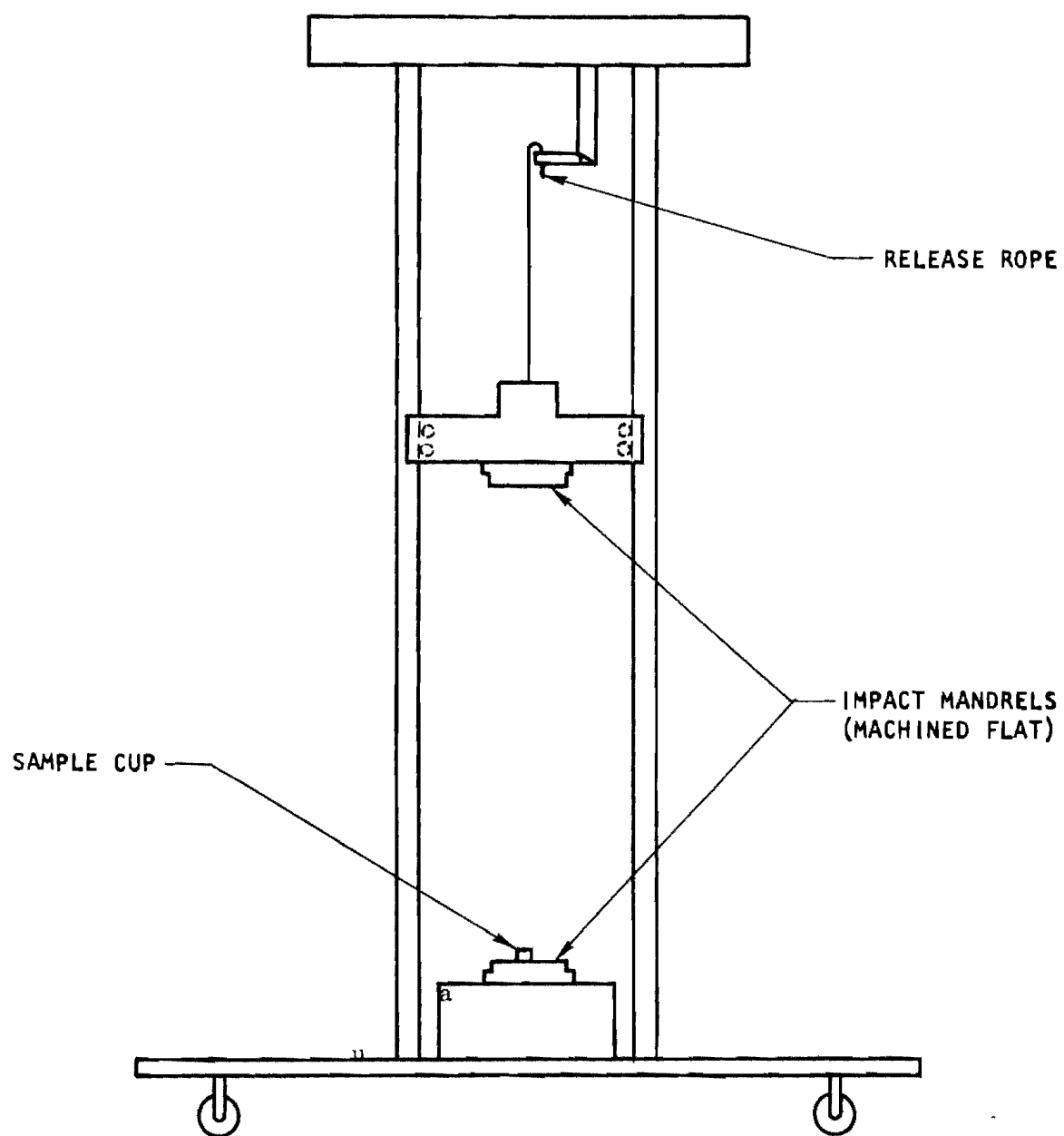


Figure 15. Drop Weight Tester

The loss of FNO_2 under test conditions was estimated from simulated tests. The simulated tests were conducted as follows:

1. A slug of the test solution approximately equal in volume to the test sample was transferred to a 10-milliliter cylinder.
2. The cylinder was conditioned to test temperature (ambient temperature for the 3 weight percent FNO_2 solution and approximately 15 F for the 9 weight percent FNO_2 solution).
3. The ullage of the cylinder was opened to the atmosphere for approximately 7 seconds, the time required to load a sample cup and conduct a drop weight test.
4. The liquid in the cylinder was analyzed.

The analysis of the 3 weight percent solution revealed that the concentration of FNO_2 in the sample cups was actually approximately 0.3 weight percent. For this reason, the 9 weight percent INTO tests were conducted at reduced temperature. It was anticipated that reduced temperature would increase the actual test concentration of FNO_2 . Analysis of the simulated test sample for the 9 weight percent solution revealed a value of 3 weight percent for the final FNO_2 concentration. Thus, approximately 70 percent of the original FNO_2 was lost to the atmosphere even at 15 F. Because 3 weight percent is the maximum FNO_2 value for INTO (1 to 3 weight percent FNO_2), the second set of drop weight tests are more significant.

RESULTS AND DISCUSSION

U-Tube Adiabatic Compression Test

No explosions occurred during any of the U-tube tests, indicating that INTO is insensitive to this type of stimulus. Previous results (Ref. 6) revealed neat NTO to be insensitive in this test.

Detonation Propagation Test

Posttest examination of the charge containers and witness plates showed that the results of all three tests were negative. The charge containers were in approximately the same condition as the container recovered from the calibration test conducted with water. These results show that INTO will not propagate a detonation in 1-inch-diameter tubing.

Drop Weight Test

The results of all tests are presented in Table 10. It can be seen that all test results were negative, i.e., no aural or visual observation either during or after the test revealed any evidence of combustion or detonation.

CONCLUSIONS

The anticipated insensitivity of INTO has been experimentally verified. With respect to the dangers of shock sensitivity, INTO handling procedures may be essentially those of NTO.

TABLE 10

DROP WEIGHT TESTS WITH 3 AND 9 WEIGHT
PERCENT FNO_2 IN NTO

Material*	Result	Comments
Butyl Rubber	Negative	Flattening of specimens with blackening of mandrels due to impressment of rubber on mandrels
Viton-A	Negative	More extreme flattening than with butyl rubber but no indication of ignition
Kynar	Negative	Extreme flattening and cracking of specimens
Teflon	Negative	Samples shattered to flakes
Kel-F	Negative	Samples shattered to flakes
Titanium 6Al-4V	Negative	Slight flattening of specimens at edges; samples imbedded in softer mandrels

*Series of five runs with each material for each solution

TASK II: STRESS CORROSION TESTS WITH MIL-P-26539 NT0,
CONTRACT F04611-67-C-0099

INTRODUCTION

It was planned that stress corrosion tests would be conducted under this task with 250 maraging steel, 2219 aluminum, and 347 stainless steel in contact with INTO (NT0 + 1 to 3 weight percent FNO_2). The tests would have been similar to those conducted with titanium under Task II of F0411-67-C-0008 (reported elsewhere in this document).

After the tanks and sample frames had been constructed, the results of the long-term corrosion tests under AF 04(611)-10809 (reported in a later section of this report) were found to indicate that a need for a water-scavenging additive for NT0 does not exist. It was decided, therefore, that this apparatus would be used to conduct ambient temperature stress corrosion tests with the two current propellant-grade NT0's: MIL-P-26539B ("brown") and MSC-PPD-2A ("green"); the specifications for these two NT0's are presented below.

NT0 SPECIFICATIONS

Constituent	Limits, Percent by Weight	
	NT0, MIL-P-26539B	Inhibited NT0, MSC-PPD-2A
N_2O_4 Assay	99.50 min	98.50 min*
NO Assay		0.8 \pm 0.20
Mositure Content Water Equivalent	0.10 max	0.10 max
Chloride as NOCl	0.080 max**	0.08 max

*The summation of N_2O_4 and NO will not be less than 99.5 percent by weight

**This test need not be performed if the propellant is manufactured by the reduction process

The tests with the former oxidizer are presented under this tank, those with the MSC-PPD-2A oxidizer are presented under Task III. The specimens were pre-notched in these tests to increase the severity of the conditions.

EXPERIMENTAL

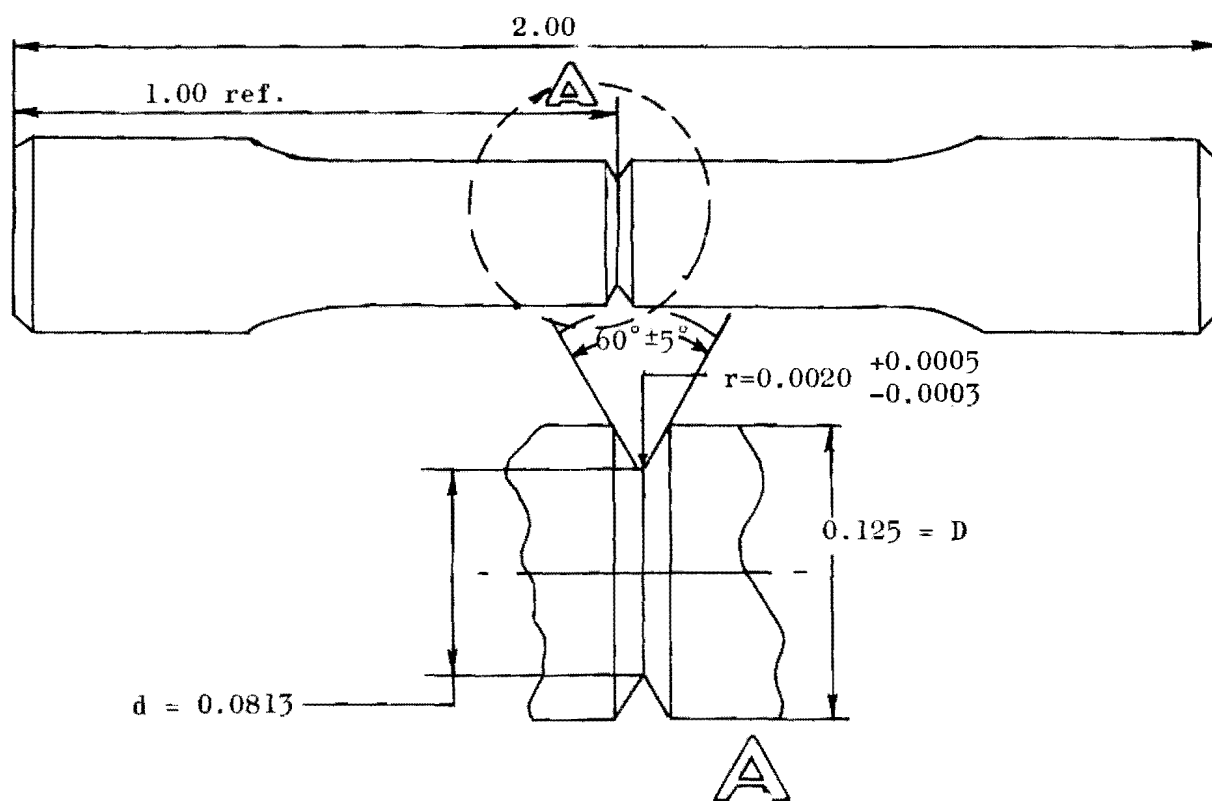
The tanks constructed to hold the propellant, specimen holders, and specimens were identical in design to the titanium tanks shown in Fig. 5. They were of 347 stainless steel, 250 maraging steel, and 2014 aluminum; the latter was used for the 2219 test specimens because tanks of this material could not be readily procured. The testing and cleaning procedures used with these tanks were the same as those described previously for the titanium stress corrosion tests.

The stress corrosion frames (Fig. 6) were of the same material as the test specimens. The notched test specimens were prepared as shown in Fig. 16. The nominal r , radius of the notch as measured after machining (Fig. 16), was 0.002, yielding a stress concentration factor, K_T , of 4.27. K_T is the theoretical elastic stress concentration and is calculated from the geometry of the notch using Fig. 25 of Ref. 8. The specimens were loaded to $2/3$ of ultimate as determined on the control samples.

The specimens were then exposed to nitrogen tetroxide meeting the requirements of MIL-P-26539 for 45 days at ambient temperatures. One half of the specimens had the notch immersed in the liquid. The other half of the specimens had the notch in the vapor phase of the tank. Radiographs of the specimens were taken on the second, sixteenth, and thirty-second day of the test.

RESULTS AND DISCUSSION

None of the specimens failed. However, as can be seen in Table 11, the aluminum alloy 2219-T6 and the maraging steel grade 250 had a decrease in ultimate strength as a result of their exposure to NT0 meeting MIL-P-26539. There was no change in the 347 stainless steel.



Stress Concentration Factor, K_T :

$$r = 0.0020$$

$$D = 0.125$$

$$d = 0.0813$$

$$K_T = 4.27 \text{ (calculated using Fig. 25 of Ref. 8)}$$

Figure 16. Notched Tensile Specimen

CONCLUSION

Notched specimens of maraging steel grade 250 and 2219 aluminum undergo a decrease in ultimate strength when exposed to MIL-P-26539 NT0 under stressed conditions but do not fail. Similar specimens of 347 stainless steel are unaffected under these conditions.

TABLE 11

STRESS CORROSION TESTS OF NOTCHED SPECIMENS OF ALUMINUM ALLOY 2219-T6,
347 STAINLESS STEEL AND 250 MARAGING STEEL EXPOSED TO NITROGEN TETROXIDE MEETING MIL-P-26539 AND
MSC-PPD-2A FOR 45 DAYS AT AMBIENT TEMPERATURES

Material	Pretest Properties				Posttest, Mil-P-26539, Properties				Posttest, MSC-PPD-2A, Properties			
	Size, inch	Area, square inch	Ultimate Load, pounds	Ultimate Strength, ksi	Size, inch	Area, square inch	Ultimate Load, pounds	Ultimate Strength, ksi	Size, inch	Area, square inch	Ultimate Load, pounds	Ultimate Strength, ksi
Aluminum 2219-T6	1. 0.082	0.0053	457	86.2	1. 0.081	0.0052	360	69.9	1. 0.081	0.0052	446	89.6
	2. 0.082	0.0053	460	86.8	2. 0.081	0.0052	330	64.0	2. 0.081	0.0052	465	89.4
	3. 0.081	0.0052	456	87.7	3. 0.081	0.0052	335	65.0	3. 0.081	0.0052	460	88.5
					4. 0.081	0.0052	300	58.2	4. 0.081	0.0052	476	91.5
					5. 0.081	0.0052	300	58.2	5.)	Broke removing from stress frames		
					6. Broke removing from stress frame				6.)			
347 SS	1. 0.082	0.0053	660	124.5	1. 0.082	0.0053	650	123.1	1. 0.082	0.0053	665	125.5
	2. 0.081	0.0052	655	125.9	2. 0.082	0.0053	640	121.2	2. 0.082	0.0053	675	127.4
	3. 0.082	0.0053	655	123.6	3. 0.082	0.0053	650	123.1	3. 0.082	0.0053	670	126.4
					4. 0.082	0.0053	650	123.1	4. 0.082	0.0053	675	127.4
					5. 0.082	0.0053	640	121.2	5. 0.082	0.0053	660	124.5
					6. 0.082	0.0053	630	119.3	6. 0.082	0.0053	675	127.4
250 Maraging Steel	1. 0.082	0.0053	2135	402.8	1. 0.082	0.0053	1700	321.9	1. 0.082	0.0053	2175	410.4
	2. 0.082	0.0053	2180	411.3	2. 0.082	0.0053	1650	312.5	2. 0.082	0.0053	2230	420.7
	3. 0.082	0.0053	2200	415.0	3. 0.082	0.0053	1650	312.5	3. 0.082	0.0053	2195	414.2
					4. 0.082	0.0053	1630	308.7	4. 0.082	0.0053	2225	419.8
					5. 0.082	0.0053	1640	310.6	5. 0.082	0.0053	2190	413.2
					6. 0.082	0.0053	1630	308.7	6. 0.082	0.0053	2210	416.9

**TASK III: STRESS CORROSION TESTS WITH MSC-PPD-2A NT0,
CONTRACT F04611-67-C-0099**

RESULTS AND DISCUSSION

These ambient temperature stress corrosion tests were identical to those described in the previous task except that the propellant was "green" NT0, MSC-PPD-2A.

None of the specimens broke during 45 days of test. It may be seen from Table 11 that no change in ultimate strength occurred with any of the alloys as a result of this exposure.

CONCLUSION

Notched specimens of maraging steel grade 250, 2219 aluminum, and 347 stainless steel are unaffected when exposed to MSC-PPD-2A NT0 under stressed conditions.

TASK IV: METAL ION ANALYSES, CONTRACT
FO4611-67-C-0099

INTRODUCTION

The objective of this task was the development of methods for the determination of trace amounts of Cr, Cu, Al, Ni, Fe and Ti in both nitrogen tetroxide (NTO) and inhibited nitrogen tetroxide (INTO) utilizing atomic absorption spectrometry. A step-wise analysis scheme to accomplish this objective has been developed and is given in detail in an appendix to this report.

In atomic absorption spectrometry, a beam of light originating from excited atoms of a particular element is passed through a portion of the sample which has been partially dissociated into atoms. Any atoms of this element in the sample absorb energy from the light beam at specific wave lengths as they are raised to higher energy states. In commercial atomic absorption spectrometers, the light source is usually a hollow cathode lamp and the sample is dissociated by aspirating the sample solution into a flame. The attenuation of the light beam from the hollow cathode lamp is a measure of the number of atoms of the element in the flame and, therefore, in the sample solution. The absorption obtained with the sample is compared to that obtained with a standard solution. As a method of analysis, atomic absorption is applicable to most metallic elements and offers the advantages of specificity and sensitivity.

The successful analysis of trace amounts of metal ions in NTO and INTO by atomic absorption spectrometry is primarily dependent upon three factors. The first is concerned with standards because there is always the possibility of matrix effects. For this reason, standards are usually made to approach the composition of the samples as closely as possible. In the case of both NTO and INTO, this condition would require the use of blanks and standards made from these materials. Because the handling of these compounds is not easy and their purity is difficult to control, standards made from NTO and INTO might prove to be impractical. Initial efforts

were, therefore, directed towards determining a simpler matrix for sample and standard solutions. The simplest matrix for analysis is water. Therefore, hydrolysis of the NT0 and INTO was investigated and found to be quite adequate. In this case, blanks and standards were made up in the appropriate percent nitric acid calculated from the amount of NT0 sample hydrolyzed.

The second factor to be considered is sensitivity. To increase sensitivity, a technique for concentrating the metal impurities was needed. To accomplish this objective, both evaporative concentration of NT0 and extraction of the hydrolyzed sample with oxine (8-quinolinol) into methyl isobutyl ketone (MIBK) was attempted. The former method was successful in increasing the sensitivity of the analysis by a factor of 20. Utilizing this technique, a much greater enhancement of sensitivity is theoretically possible. The extraction method was far less successful and was also very time consuming. The investigation of the extraction technique was therefore abandoned after preliminary experiments.

A third factor and perhaps one of the most important factors in any successful analysis is recovery; i.e., adding known amounts of the elements of interest to the sample and obtaining these exact amounts or very close to these amounts upon analysis. Therefore, a considerable portion of the effort was expended on investigating recovery of Cr, Cu, Al, Ni, Fe, and Ti in NT0.

EXPERIMENTAL AND RESULTS

NT0 Analysis

Hydrolysis Technique. This technique consisted of the hydrolysis of a known amount of nitrogen tetroxide by addition to excess frozen deionized water and allowing the mixture to warm to room temperature. Hydrolysis of NT0 resulted in the formation of nitric acid and nitrous acid. The latter is unstable and the NO gas effervescing from the hydrolysis solution was found to interfere with the aspiration of the sample during the analysis

by atomic absorption. Therefore, the hydrolysis solution was heated to ~90 C prior to analysis to destroy the nitrous acid. A series of experiments were run on distilled NT0 and NT0 with known amounts of added metal ions to determine the percent recovery.

Samples of NT0 containing known amounts of added metals were prepared as follows. An appropriate amount of the aqueous standard solution was micro-pipetted into a 15-milliliter graduated centrifuge tube fitted with a Fischer-Porter (FP) valve. The centrifuge tube was placed on the sampling line (Fig. 17) by means of a ball and socket joint with a minimum amount of silicone grease. The line was opened from the vacuum pump up to the NT0 supply and the excess water in the centrifuge tube was carefully evaporated by slowly opening FP valve No. 3 and submersing the tip of the tube in warm water. Care was taken to avoid bumping. In each series of runs, one sample of distilled NT0 was run as a blank. After removal of the excess water, FP valve No. 1 was closed and FP valve No. 2 was opened allowing NT0 to flow into the centrifuge tube. If flow did not occur, a piece of ice was placed against the side of the tube to lower the NT0 vapor pressure in the tube and initiate flow. When 10 milliliters of NT0 had been drawn into the centrifuge tube, FP valves No. 2 and 3 were closed and the excess NT0 was pumped into the -78 C trap. The centrifuge tube was removed from the sampling line and shaken approximately 1 minute to ensure mixing.

The tube was then inverted over a cylindrical container of approximately 100-milliliter capacity fitted with a ball and socket joint cap that contained 50 milliliters of frozen deionized water. In the case of aluminum, 43 milliliters of deionized water and 7 milliliters of a 20,000-ppm potassium solution were used to prevent ionization interference as is recommended by the manufacturer of the atomic absorption spectrophotometer. The ball and socket cap was secured loosely on the container and the contents were allowed to warm slowly. When the ice had completely melted, three washings from the centrifuge tube of approximately 3-milliliter volume each were added to the container. When the solution reached room temperature, the container was placed in a hot water bath (~90 C) and maintained in the bath until the solution was one phase and vigorous bubbling had ceased.

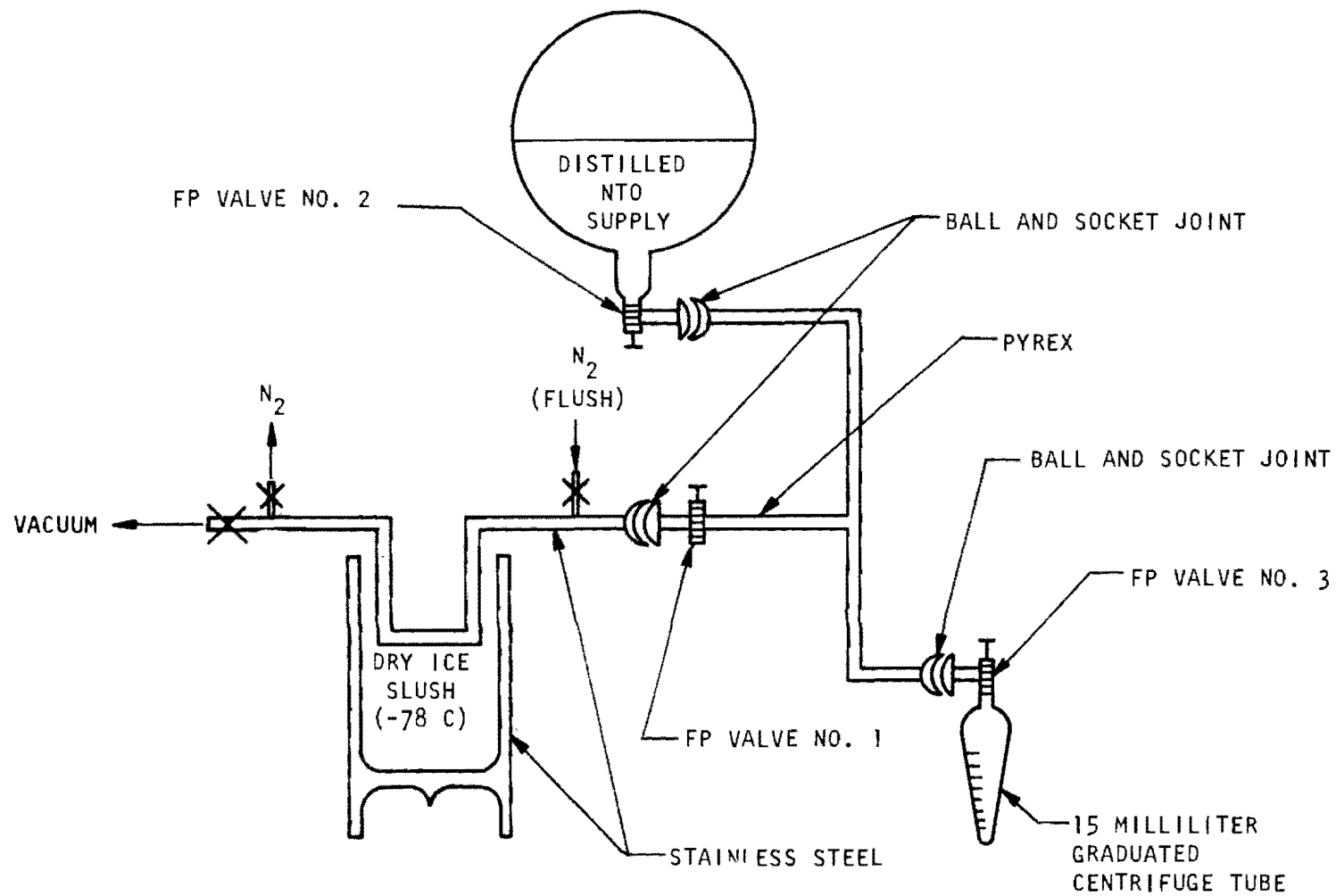


Figure 17. NTO Sampling System

When the solution cooled to room temperature, the liquid level was marked on the side of the container and the solution was analyzed on a Perkin-Elmer model 303 atomic absorption spectrometer versus standards. The latter were prepared from the same stock solution as was used to dope the sample, and was 10 volume percent in nitric acid. After analyzing the solution, the initial volume was measured by using a buret to fill the container to the mark made prior to the run. The volume obtained was used to calculate the percentage recovery of the element of interest.

The results of this series of analysis are presented in Table 12. The detection limits listed in the last column were estimated from the observed noise level and the minimum absorption which could be read accurately. Some of the reported analyses approached the limit of detection.

To determine if there were any interelement effects that would give erroneous results, samples of NT0 were doped with all six elements simultaneously and analyzed by the same procedure utilized previously, except that all solutions and standards were 2000 ppm in potassium to obviate ionization interference in the case of aluminum. The overall average recovery for all of the elements was 90 ± 20 percent.

Four-Fold Evaporative Concentration of NT0. Forty milliliters of NT0 which had been spiked with Al, Cr, Cu, Fe, Ni and Ti were slowly evaporated until 10 milliliters remained. The 30 milliliters that were removed were collected in three equal portions in 15-milliliter graduated centrifuge tubes fitted with Fischer-Porter valves. The residue and the three distillate fractions were hydrolyzed and analyzed by atomic absorption spectrometry by the same procedure utilized previously. The final volume of the hydrolyzed sample was about 70 milliliters.

Significant amounts of the metals were found only in the residue. The data are presented in Table 13. Examination of Table 13 reveals that although overall the recoveries were fair, there were some unexplainable discrepancies, particularly the low (68 percent) Cr recovery. Therefore, a second four-fold

TABLE 12

ANALYSIS OF HYDROLYZED NTO SAMPLES

Element	Amount Added, micrograms	Amount Recovered, micrograms	Percent Recovery	Detection Limit,* μg/ml NTO
Al	200	178	89	4
Al	250	231	92	
Cr	50	Lost in Processing		0.2
Cr	100	92	92	
Cu	50	47	94	0.2
Cu	100	103	103	
Ni	50	46	92	0.4
Ni	100	100	100	
Ti	60	75	125	6
Ti	120	127	106	
Fe	Based on Previous Work			0.2**
Average Overall Percent Recovery = 99 ±11 percent (standard deviation)				

*Detection limits refer to neat NTO (10-milliliter NTO sample and 70-milliliter final volume)

**Work accomplished under Contract AF 04(611)-11620 (Ref. 9)

TABLE 13

FOUR-FOLD EVAPORATIVE CONCENTRATION ANALYSIS

Element	Amount Added, micrograms	Percent Recovery				Detection ^a Limit, μg/ml NTO
		Distillate Fractions			Residue	
		1	2	3		
Al	1000	6	6	7	105	1
Cr	40	<0(0) ^{b,c}	<0 ^b	<0 ^b	68(85) ^c	0.06
Cu	40	0	4.8	3.3	93	0.06
Ni	100	0	0	0	100	0.1
Ti	600	0	0	0	101	1.5
Fe	40	4.8	6.5	6.5	105	0.05

^aDetection limits refer to original 40-milliliter neat NTO solution.

^bThe blank had a slightly higher absorption than fractions 1, 2, and 3.

^cValues in parentheses were obtained by adjusting the absorbance of the distillate fraction 1 to zero.

concentration experiment was performed reducing the amount of dopant added by a factor of five. In this experiment only the first and third distillate fractions were analyzed along with the residue. Again significant amounts of the metals were found only in the residue. The data are presented in Table 14.

The data (Table 14) were examined to determine whether the levels of concentration of the various metals in the hydrolyzed solutions were sufficiently high to provide accurate results. When the NT0 residue was hydrolyzed and heated to 90 C to remove the bulk of the nitrous acid, the final volume of the solution was 45 milliliters. Assuming 100 percent recovery in the residue, the concentration of metals in the hydrolyzed residue should be: Cu, 0.18 $\mu\text{g/ml}$; Fe, 0.18 $\mu\text{g/ml}$; Cr, 0.18 $\mu\text{g/ml}$; and Ni, 0.05 $\mu\text{g/ml}$. The detection limits reported by the instrument manufacturer for the four metals are: Cu, 0.005 $\mu\text{g/ml}$; Fe, 0.05 $\mu\text{g/ml}$; Cr, 0.01 $\mu\text{g/ml}$; and Ni, 0.05 $\mu\text{g/ml}$. The detection limit is defined as the concentration of sample in solution giving a signal twice as large as the background variability. It is seen that the sample was doped with slightly less Ni than the literature-reported detection limit for nickel. Therefore, the nickel values are not as accurate as those of the other metals. The levels of the other metals were sufficiently high for accurate results.

The percent recovery of Fe, Cu, and Ni was good at these low concentrations (Table 14). However, chromium again showed a low recovery, 74 percent. At this point, it was felt that this low recovery may have been due to chemical depression occurring during the atomic absorption analysis. The instrument manufacturer has reported that chromium is one of several elements that can be chemically depressed. This phenomenon occurs when species that reduce the absorption of the atomized element are present in the unknown but not in the standards. This would tend to indicate that there are apparent chemical differences between solutions prepared in 10-percent HNO_3 and those prepared by hydrolyzing NT0 to form a HNO_3 solution. However, in the next experiment involving a twenty-fold concentration of NT0, the chromium recovery was higher, 89 percent.

TABLE 14

FOUR-FOLD EVAPORATIVE CONCENTRATION
ANALYSIS, RUN 2

Element	Amount Added, micrograms	Percent Recovery		
		Distillate Fraction		Residue
		1	3	
Fe	8	0	0	91
Ni*	2	0	0	91
Cu	8	0	<0**	102
Cr	8	0	0	74

*Inadvertently, 2 instead of 20 micrograms of Ni were added.

**The blank had a slightly higher absorption than this fraction.

Twenty-Fold Evaporative Concentration of NT0. One hundred milliliters of NT0 which had been spiked with Fe, Ni, Cu, Cr, Al, and Ti were carefully evaporated until a 5-milliliter residue remained. The first 90 milliliters were collected and set aside. The last 5 milliliters of NT0 distillate were collected, hydrolyzed, and analyzed along with the 5-milliliter residue. The analysis was conducted in the same manner as described in the four-fold concentration. It was observed that some solid material did not dissolve even after hydrolysis, and therefore some low recoveries were expected. The results are summarized in Table 15. They show that the insoluble material was not a major factor in the recovery of the metals.

As indicated in Table 15, aluminum and chromium to a lesser extent, were the only metals which appeared in the distillate. The detection limits reported by the instrument manufacturer for these two metals are: aluminum, $0.5 \mu\text{g/ml}$ and chromium, $0.01 \mu\text{g/ml}$. Because the final volume of the hydrolyzed distillate was 41 milliliters, the 3-percent (21 micrograms) aluminum detected in the distillate is equal to its detection limit and may therefore be considered within experimental error. The 0.7-percent (7 micrograms) Cr in the distillate resulted in a solution which was an order of magnitude above the detection limit in the hydrolyzate (0.7-percent chromium represents $0.2 \mu\text{g/ml}$). Thus, it seems possible that a small portion of the chromium may have been carried over into the distillate.

The recovery of titanium in the residue was 94 percent. The 6 percent "loss" is below the detection limit for titanium in the hydrolyzed solution. Six percent (36 micrograms) of the titanium is the equivalent of $0.5 \mu\text{g/ml}$ in the hydrolyzed solution. The detection limit for titanium as reported by the instrument manufacturer is $1.0 \mu\text{g/ml}$. Therefore, the recovery of titanium is within experimental error.

The recoveries of Fe, Ni, Cu, Cr, and Al are 94, 96, 92, 89, and 87 percent, respectively (Table 15). The "losses" of these five metals are all above the order of magnitude of the detection limits of these elements in the hydrolyzed solution. As previously mentioned, a small amount of the doping

TABLE 15

TWENTY-FOLD EVAPORATIVE CONCENTRATION ANALYSIS

Element	Amount Added, micrograms	Percent Recovery	
		5-Milliliter Distillate Prior to Residue	5-Milliliter Residue
Fe	1000	0	94
Ni	2000	0	96
Cu	1000	0	92
Cr	1000	<0.7	89
Al	700	3	87
Ti	600	0	94

mixture remained in the centrifuge tube, undissolved. This may well account for these small losses. From the previous results, it can be concluded that a twenty-fold concentration of metals in NTO has been successfully demonstrated by evaporation techniques.

Extraction Technique. An attempt was made to develop an extractive technique to increase the sensitivity of the analysis. The plan was to extract the metal ions from hydrolyzed NTO samples buffered at a pH of 5 into either CHCl_3 or methylisobutylketone (MIBK) containing 1-percent oxine (8-quinolinol) as the complexing agent. Then, if necessary, a further extraction into MIBK was to be made using acetyl acetone as the complexing agent. The resulting solutions were then to be analyzed by one of the following two methods:

1. Analysis after conversion to an HNO_3 solution
 - a. Evaporate organic solvent just to dryness
 - b. Dissolve in concentrated HNO_3
 - c. Transfer to volumetric flask and dilute to volume with deionized H_2O
 - d. Analyze by atomic absorption using 10-percent HNO_3 solutions of the metals as standards
2. Analysis in Organic Solvent
 - a. Dilute organic layer to volume in volumetric flask
 - b. Prepare standards in 10-percent HNO_3
 - c. Extract standards using same procedure as used for the samples
 - c. Dilute extracted standards (organic layer) to volume in volumetric flask
 - e. Analyze by atomic absorption

The first set of samples analyzed by the extraction technique were made up by doping 10-percent HNO_3 solutions with appropriate amounts of the six elements of interest. The solutions were then buffered to pH 5 and

extracted using MIBK solvent first with oxine and later with acetyl acetone as complexing agents. The atomic absorption analysis was carried out utilizing Method 1. The results of this analysis are shown in Table 16. Relatively good results were obtained for all elements except titanium.

The second set of samples analyzed by the extraction technique was prepared by doping NTO samples with the six elements of interest, hydrolyzing them as described previously, and then proceeding as above. Method 2 was used for the atomic absorption analysis. The results are presented in Table 17. Examination of the data reveals that the hydrolyzed NTO sample did not extract nearly as well as did the 10 percent HNO_3 solution. The reason for this difference is not immediately apparent because the hydrolyzed NTO solution should contain approximately 10 percent HNO_3 . A possible explanation might be competitive complexing of the metal ions by NO present in the hydrolyzed NTO solutions. Because of the success of the evaporative concentration technique described in the previous subsection of this report, no further investigation of this interesting phenomenon was made.

INTO Analysis

Hydrolysis Technique. One set of three 10-milliliter INTO samples consisting of a blank and two samples doped with different amounts of all of the elements of interest was hydrolyzed and analyzed. All operations were conducted in Teflon laboratory ware because of the HF present in the hydrolyzed sample. Exceptionally high results for all of the metals particularly Fe and Cr were obtained. These INTO samples were obtained directly from 304 stainless-steel storability samplers.

It was thought that part of the trouble might have been due to the presence of particulate metal fluoride that might have been washed into the sampling container along with the INTO. An analysis scheme which would eliminate this possibility was therefore devised and carried out.

TABLE 16

ANALYSIS OF EXTRACTED HNO_3 SAMPLES*

Element	Amount Added, micrograms	Amount Recovered, micrograms	Percent Recovery	Solvent	Extractants (at pH of 5)
Cu	0	16.5	--	CHCl_3	Oxine
	16	16.5	0		
	40	38.8	56		
	0	7.5	--	MIBK	Oxine-Acetyl Acetone
	16	23.0	97		
	40	45.5	95		
Ni	0	0	--	CH_2Cl_3	Oxine
	40	38	95		
	100	94	94		
	0	1	--	MIBK	Oxine-Acetyl Acetone
	40	43	105		
	100	102	101		
Fe	0	2.8	--	CHCl_3	Oxine
	16	22.8	125		
	40	37.3	86		
	0	4.8	--	MIBK	Oxine-Acetyl Acetone
	16	18.8	88		
	40	35.0	76		
Cr	0	3.8	--	CHCl_3	Oxine
	16	7.3	22		
	40	11.0	18		
	0	8.0	--	MIBK	Oxine-Acetyl Acetone
	16	21.5	84		
	40	38.8	77		
Ti	0	0	--	CHCl_3	Oxine
	300	153	51		
	600	293	49		
	0	2.5	--	MIBK	Oxine-Acetyl Acetone
	300	170	56		
	600	340	56		

*Two sets of HNO_3 samples, each consisting of a blank plus two samples doped with all of the metals

TABLE 16
(Concluded)

Element	Amount Added, micrograms	Amount Recovered, micrograms	Percent Recovery	Solvent	Extractants (at pH of 5)
Al	0	0	--	CHCl ₃	Oxine
	500	450	90		
	1000	830	83		
	0	5	--	MIBK	Oxine- Acetyl Acetone
	500	475	94		
	1000	820	82		

TABLE 17

ANALYSIS OF EXTRACTED HYDROLYZED NTO SAMPLES*

Element	Amount Added, micrograms	Amount Recovered, micrograms	Percent Recovery
Cu	0	0.35	--
	8	3.7	46
	16	3.1	19
Ni	0	0	0
	20	0	0
	40	0	0
Fe	0	**	--
	8	**	--
	16	**	--
Cr	0	<0***	--
	8	<0***	--
	16	0	0
Ti	0	0	0
	150	1.3	0.9
	300	2.3	0.8
Al	0	0	--
	250	203	81
	500	316	63

*One set of a blank plus two NTO samples doped with all of the metals

**Standards and solvents had become badly contaminated during handling, perhaps because of the use of a Teflon-clad iron stirring bar

***The blank had a slightly higher absorption than this sample.

Three samples of INT0 which had been used for storability tests in A286 steel were analyzed by this improved analysis scheme. Two of the samples were analyzed as received, one was hydrolyzed in glass and the other in Kel-F equipment. The third sample was doped with the elements of interest and hydrolyzed in Kel-F. Because the storability containers were only 20 cubic centimeters in volume, it was necessary to use three different samples from separate A286 steel containers for analysis. Therefore, the data from the spiked INT0 sample cannot be used as quantitative recovery data for Fe, Ni and Cr, because the initial amounts present before spiking are unknown.

The INT0 samples were transferred directly into a Kel-F graduated cylinder from the A286 steel container through a 325-mesh stainless-steel screen to remove particulate matter. The amount of INT0 transferred was determined by weighing the container before and after transfer. The sample was then poured into a Kel-F bottle containing 40 milliliters of frozen deionized water. After hydrolysis and heating to remove HNO_2 , the solutions were analyzed by atomic absorption spectrometry. In the case of the spiked sample, the dopant was added to the Kel-F graduate prior to the introduction of the sample.

The results are shown in Table 18, 19, and 20. Table 18 lists the results of the analysis on the as received sample, hydrolyzed in glass. Table 19 lists the results of the analysis of an as received sample performed entirely in Kel-F laboratory ware. The results in Tables 18 and 19 are similar except that Table 19 shows no spurious Al since a Kel-F cylinder was used. They do, however, indicate small variations in the level of Fe, Cr, and Ni found from different samplers. The results in Table 20 show a nearly quantitative recovery of Cu, Ti, and Al. The recovery of Fe, Cr, and Ni cannot be determined exactly because the amounts present before doping could not be determined from the limited amount of sample available; however, this correction would lower the Fe and Ni recoveries even further.

TABLE 18

ANALYSIS OF INTO FROM A286 STEEL CYLINDER

Element	μg Found in Hydrolyzate	ppm in INTO
Cu	6	0.2
Fe	24	1.1
Cr	15	0.65
Ni	6	0.65
Ti	0	0.2
Al	964*	--

*Aluminum resulted from attack on the glass hydrolysis vessel

TABLE 19

ANALYSIS OF INTO FROM A286 STEEL CYLINDER

Element	μg Found in Hydrolyzate	ppm in INTO
Cu	2	0.1
Fe	42.8	2.2
Cr	28.5	1.5
Ni	19.0	1.0
Ti	0	0
Al	0	0

TABLE 20

ANALYSIS OF INTO WITH ADDED METAL IONS

Element	μg Added	μg Found in Hydrolyzate	ppm in INTO	Percent Recovery
Cu	100	87.4	4.7	83
Fe	100	101.2	5.4	75*
Cr	100	133.4	7.2	109*
Ni	200	165.6	8.9	78*
Ti	600	607	13.2	101
Al	500	492	10.7	99

*These values can only be approximate for reasons given in text.

CONCLUSIONS

Atomic absorption methods have been developed to analyze NT0 and INT0 for dissolved metals. Four-fold and twenty-fold evaporative concentrations of dissolved Cr, Cu, Al, Ni, Fe, and Ti in N_2O_4 were accomplished to increase the sensitivity of the method. Utilizing the techniques developed, a great enhancement of sensitivity is deemed feasible.

The hydrolysis technique followed by analysis by atomic absorption spectrometry offers a simple, rapid and specific method for the determination of trace metals in both NT0 and INT0. Not only is operator time at a minimum, but there also is no lengthy elapsed time in this procedure. Good recoveries of Cu, Fe, Ni, Cr, Ti, and Al were obtained at two vastly different concentration levels and by two analysts, thus indicating the reliability of the method.

INHIBITED N_2O_4 , CONTRACT AF 04(611)-10809

A program to evaluate the liquid oxidizer INT0, which is NT0 inhibited by a fluorine oxidizer, was conducted under Contract AF 04(611)-10809. The results obtained during the first 15 months of that program were reported in AFRPL-TR-66-320 (Ref. 5). This section of this report presents the results of the long-term corrosion and storability tests conducted under AF 04(611)-10809, and is a supplement to the previously submitted final report (Ref. 5).

In addition to the corrosion and storability tests reported herein, Ref. 5 presents results in the following areas: corrosive effects of flowing INT0, transfer effects with INT0, electrical conductivity of NT0 and INT0, reclamation of out-of-specification NT0, field preparation of INT0, vapor pressure and freezing point of $FN0_2$ /NT0 mixtures, and development of methods for the chemical analysis of NT0 and INT0.

TASK I: COUPON CORROSION TESTS

INTRODUCTION

The primary purpose of replacing NT0 with INT0 is to eliminate corrosion in field-use systems, or at least to reduce it to acceptable limits. Evaluation of improvements must be based on studies of the corrosive effects of INT0 compared to the corrosive effects of NT0 on the metal alloys used in propellant-handling systems. A limited series of screening tests were performed to evaluate the efficiency of the inhibitor.

Literature data available at the start of this program (Ref. 1 through 4 and 10) indicated that corrosion rates of the alloys of interest varied between 0.01 and 2.2 mils per year with NT0 containing 0.3 weight percent water (the water content of one of the NT0 samples used in this program). One report (Ref. 2) described wet NT0 as being as corrosive as 60-percent nitric acid.

Table 21 summarizes the available corrosion rates at 0.3-percent water for four of the alloys used in this program. These rates were based on tests ranging in length from 3 to 27 days and were extrapolated to mils per year. It was apparent that long-term corrosion tests (1 to 2 years) with NT0 and INT0 would be required to establish the magnitude of the wet NT0 corrosion problem and the improvement obtained with INT0.

EXPERIMENTAL

Materials

Alloys. An inspection of the materials in the Titan II engine system showed that an extremely large number of alloys are required for even this single application. It was far beyond the scope of this effort to evaluate the corrosion resistance of all of these materials to INT0. Instead, representative alloys were selected for testing. These materials are listed in Table 22.

TABLE 21

SUMMARY OF LITERATURE DATA ON CORROSIVITY OF WET NTO
(0.3 Weight Percent Water)

Material	Test Duration, days	Corrosion, mils per year	Temperature, C	Reference
304L	3 to 27	0.01 to 0.03	21	4
2024 Al	7	2.0	38	3
7075 Al	7	2.2	38	3
Carbon Steel (ASTM-A285)	3 to 27	0.03 to 0.18	21	4

TABLE 22

MATERIALS SUBJECTED TO CORROSIVITY TESTING

Group I Iron Alloys	Group II Aluminum Alloys
304L Stainless Steel	6061-T6
316 Stainless Steel	7075-T73
321 Stainless Steel	Tens-50
AM350 SCT	2014-T6
440C Stainless Steel	2024
1018 Carbon Steel	
Welded specimens of all the above	Welded specimens of 6061, Tens-50, and 2014

Propellants. Because the investigation was basically comparative in nature, specimens were exposed to five different propellant compositions. These were:

1. MS NT0*, military specification P 26539A, less than 0.1 weight percent H_2O equivalent and a minimum 99.5 percent assay
2. Wet NT0*, MS NT0 with water added to a 0.33 weight percent H_2O equivalent
3. Dry INT0*, prepared from specially dried NT0 (<0.01 weight percent H_2O equivalent) and containing 1 to 3 weight percent $FN0_2$
4. Wet INT0*, prepared from wet NT0 (0.22 weight percent H_2O equivalent) and containing 1 to 3 weight percent $FN0_2$
5. Dry NT0 + HF*, prepared from specially dried NT0 (<0.01 weight percent H_2O equivalent) and containing 0.1 to 0.5 weight percent HF

These compositions broadly cover the conditions that could be expected in actual operations. The fifth composition was included to check the effect of the major reaction product between the additive and water in the absence of either of these materials.

Solutions 3 and 5 were prepared by drying commercial NT0 and then adding known amounts of the desired additives. The NT0 was dried by reacting commercial NT0 with P_2O_5 , pressurizing the reaction mixture to 30 psi with O_2 to oxidize the N_2O_3 formed by the drying process, and then distilling off the resulting dry NT0. Water content was determined by nuclear magnetic resonance (NMR), aluminum Turner bulb, or phase separation analysis. HF and $FN0_2$ contents were determined by infrared spectroscopy. The propellant was loaded into the test bombs in a closed transfer system (on a vacuum line). The technique is discussed in detail elsewhere (Ref. 5).

*For brevity, these descriptive terms will be used throughout the remainder of this report when referring to these five solutions.

Preparation of Specimens and Test Cylinders

The testing procedure was designed so that both welded and nonwelded specimens would be exposed to both the liquid propellant and propellant vapor for each of the compositions. Materials were tested by exposing small disks (approximately 1/16 inch thick, 7/8 inch diameter, 2.9 square inch area) to the propellants. Aluminum disks weighed on the average 0.8 gram and iron disks 3 grams. These disks were strung on rods and were separated by Teflon spacers (Fig. 1 of Ref. 5). The spacers minimized interaction between individual specimens and ensured free access of the propellant to the surface of the specimens. Kel-F disks were placed between specimens to catch any residue that might have fallen off the surface of the specimens during testing. For material uniformity, aluminum alloy specimens were strung on aluminum rods, and iron alloy specimens on stainless-steel rods.

Tests were conducted in stainless-steel and aluminum cylinders which were capped on one end and valved on the other end. Steel valves were used on the stainless-steel test cylinders, and aluminum valves were used on the aluminum test cylinders.

Uniformity of specimens of each material was assured by cutting a sufficient number of specimens to perform all tests from a single piece of stock. Any heat treatment, cleaning, or other preparatory operations were performed on the original stock before cutting the specimens. All specimens were cleaned with a soap solution, rinsed with water and acetone and weighed before testing. Each specimen was also stamped with a number and a letter, designating the test condition and alloy, respectively.

The test cylinders, valves, and fittings were vapor-degreased, washed with soap and water, and rinsed with water, trichloroethylene, and acetone. Valves were completely disassembled for cleaning and reassembled using Fluorolube as a lubricant on the valve stem assemblies.

Testing

Three series of tests were conducted: 30-days exposure at ambient temperature (55 to 90 F), 30-daysexposure at 70 C, and 21-months exposure at ambient temperature (25 to 115 F). The results of the 30-day tests were previously reported (Ref. 5), but are repeated in this report for convenience.

All cylinders were stored in an inverted (valve down) position in an outdoor bay at the Rocketdyne Canoga Park facility. The cylinders for the elevated temperature tests were stored in an oven at 70 ± 3 C.

Periodic samples were taken of the liquid contents of all cylinders containing HF or FNO_2 . The procedure was as follows: The test cylinder was attached in an inverted position to a vacuum line to which a gas sampling cell was also attached. The sampling system was evacuated and then passivated with 20/80 FNO_2 /NT0 vapors. After evacuating the FNO_2 from the system, the valve on the test cylinder was barely opened, expanding a liquid sample to the gas phase in the sampling system. At the desired pressure (200-mm Hg), the test cylinder valve was closed to isolate the infrared or near infrared sample cell which was removed from the system and analyzed, as previously described (Ref. 5).

Unloading of Test Cylinders

Unloading procedures were designed to preserve the condition of the specimens as they were upon removal from the test cylinder.

The unloading procedure used for the wet and dry NT0 tests was as follows: After dumping the liquid from the test cylinders, the specimen strings were rapidly placed in a dry nitrogen atmosphere. When the strings of coupons no longer showed signs of degassing NT0, they were removed from the nitrogen atmosphere and given three rinses: methanol, 50-percent

methanol/50-percent water, and water. The purpose of the rinses was to remove any residual nitric acid which would continue to corrode the specimens. The specimens were then removed from the rods, blotted dry, and weighed. This procedure did not work perfectly. Flaking off of corrosion layers and a small amount of rusting occurred with the 440 C steel and 1018 carbon steel specimens.

The unloading procedure used for the other tests was as follows. After dumping the liquid from the test cylinders, the cylinders were blown out with dry nitrogen and opened in a dry box purged by moisture-free gaseous nitrogen. The dry box is approximately 4 by 3 by 3 feet with an antechamber which enables hardware to be placed into and removed from the box while maintaining an inert atmosphere. A Mettler balance was placed in the box enabling the weighings to be made in an inert atmosphere. The only work conducted in the open was the dumping of the liquid, the gaseous nitrogen purging of the INTO test cylinders, and the photographing of some specimens. All weighing and removal of the samples from the rods was conducted in the dry box. The unloading procedure proved satisfactory for all tests.

Each specimen was weighed before and after testing. The weight changes reported are averages based on four samples of each alloy (one welded and one nonwelded in both the vapor and liquid phase). The weighing error is approximately ± 0.2 milligrams.

RESULTS AND DISCUSSION

Three significant types of information were obtained from the coupon corrosion tests. The first type of information was obtained by periodically analyzing the liquid in the test cylinders for FNO_2 and HF content. A gradual decrease in additive concentration would indicate continuous reaction

with the test coupons or the test cylinder. The second type of information was obtained by visually examining the specimens for corrosion and passivation layers and by subjectively determining the adherence and toughness of possible passivation layers by tapping and scratching them. The third type of information was obtained by weighing the specimens to determine their weight gains or losses if any. The decision as to whether a layer was evidence of corrosion or of passivation was made by considering the results of the visual examination and by comparing the weight changes of specimens exposed to particular propellant compositions for 21 months to the weight changes of similar specimens exposed to the same propellant compositions for 1 month.

To aid in the analysis of the data, a weight gain ratio, WGR, was defined as being equal to the ratio of the average weight gain after 21 months for a particular alloy to the corresponding average weight gain after 1 month for the same alloy. A WGR of 21 indicates continuous reaction (corrosion) at a steady rate, whereas a WGR of 1 indicates no further reaction (passivation) after the first month. WGR's intermediate between these values could indicate either continuous reaction at a slowing reaction rate, probably due to slow diffusion through the corrosion layer, or that passivation took place but in somewhat more than 1 month. Intermediate WGR's were found to fall in two rather distinct ranges, 1.5 to 4 and 9 to 10. These were interpreted as indicating slow passivation (longer than 1 month) and decreasing reaction rate, respectively; this would appear to give a reasonable interpretation of the observed results but must be considered as somewhat speculative. WGR's of greater than 21 would indicate an increase in reaction rate after the first month of storage.

All of the data obtained in the coupon corrosion tests are presented in Tables 23 through 28. Tables 23 and 24 contain the results of the periodic analyses of the liquid contents of the test cylinders. Table 25 gives the results of the visual inspection of the test coupons after termination

TABLE 23

ANALYSES OF LIQUID CONTENTS OF TEST CYLINDERS FOR HF
DURING COUPON CORROSION TESTS

Material	HF Content (Weight Percent)			
	Initial	4 Months	18 Months	21 Months
Aluminum	0.4	0.3	0.2	0.2
Stainless Steel	0.4	0.2	0.2	0.2

TABLE 24

ANALYSES OF LIQUID CONTENTS OF TEST CYLINDERS FOR FNO_2
DURING COUPON CORROSION TESTS

Material	Original NTO Status	FNO_2 Content (Weight Percent)				
		Initial	2 Months	12 Months	18 Months	21 Months
Aluminum	Wet ^a	3	0(3) ^c	3	2	3
	Dry ^b	3	0(3) ^c	2	1	2
Stainless Steel	Wet ^a	3	2	3	3	2
	Dry ^b	3	3	2	2	2

^a0.22 weight percent water

^b<0.01 weight percent water

^cReloaded to values in parenthesis

TABLE 25

SUMMARY OF VISUAL APPEARANCES OF 21-MONTH CORROSION TEST COUPONS

Material	Phase	Appearance ^a of Coupon Surface				
		MS NT0 ^b	Wet NT0 ^b	Dry NT0+HF ^b	Dry INT0 ^b	Wet INT0 ^b
Iron Alloys						
304L SS	Liquid	u	sd	vvvtc	vtc	lc
304L SS	Vapor	u	sd	vvtc	vtc	ac
316 SS	Liquid	u	sd	vvtc	vvtc	tac
316 SS	Vapor	u	sd	vvtc	tc	tac
321 SS	Liquid	u	sd	vvtc	vtc	ac
321 SS	Vapor	u	sd	vvtc	vtc	tac
AM350	Liquid	d	d	tc	ac	slc
AM350	Vapor	d	d	tc	ac	slc
440C	Liquid	hGc	hGc	tGc	hGc	1/2g-1/2Gc
440C	Vapor	hGc	hGc	hGc	hGc	1/2g-1/2Gc
1018	Liquid	yd	yd	tGc	ac	tac
1018	Vapor	yd	yd	tGc	tac	tac
Aluminum Alloys						
Tens-50	Liquid	u	vtc	ac	lc	vlc
Tens-50	Vapor	u	vtc	ac	lc	vlc
2014	Liquid	u	u	tac	vac	lc
2014	Vapor	u	u	tac	vac	ac
2024	Liquid	u	u	tac	vac	lc
2024	Vapor	u	u	tac	vac	ac
6061	Liquid	u	u	vtac	vac	ac
6061	Vapor	u	u	tac	vac	ac
7075	Liquid	u	u	tac	vac	lc
7075	Vapor	u	u	tac	vac	ac

^aCode: l = loose, a = adherent, t = thin, h = heavy, s = slightly, u = unaffected,
c = coat, g = green, G = gray, y = yellow, d = discolored, v = very

^bThe test liquids are described on page 85.

TABLE 26

SUMMARY OF WEIGHT CHANGE OF CORROSION COUPONS

Material	Weight Changes, grams														
	MS NT0 ^a			Wet NT0 ^b			Dry NT0 ^c + HF			Dry INT0 ^c			Wet INT0 ^d		
	Ambient Temperature		70 C	Ambient Temperature		70 C	Ambient Temperature		70 C	Ambient Temperature		70 C	Ambient Temperature		70 C
	1 Month	21 Months	1 Month	1 Month	21 Months	1 Month	1 Month	21 Months	1 Month	1 Month	21 Months	1 Month	1 Month	21 Months	1 Month
Iron Alloys															
304L SS	+0.0001	0	+0.0001	+0.0002	-0.0001	-0.0046	+0.0006	+0.0004	+0.0039	+0.0011	+0.0011	+0.0006	+0.0008	+0.0357	+0.0166
316 SS	-0.0002	-0.0001	-0.0001	-0.0002	-0.0001	-0.0052	+0.0006	+0.0005	+0.0050	+0.0005	+0.0008	0	+0.0004	+0.0068	+0.0088
321 SS	+0.0001	-0.0003	+0.0002	-0.0002	-0.0002	-0.0054	+0.0010	+0.0006	+0.0056	+0.0006	+0.0007	+0.0003	+0.0006	+0.0218	+0.0122
AM 350	0	-0.0005	+0.0001	-0.0001	-0.0005	-0.0077	+0.0023	+0.0022	+0.0088	+0.0018	+0.0035	+0.0026	+0.0021	+0.0331	+0.0376
440C	-0.0002 ^e	-0.0004 ^e	+0.0016 ^e	-0.0006 ^e	+0.0003 ^e	-0.0222 ^e	+0.0048	+0.0133	+0.0447	+0.0021	+0.0180	+0.0280	+0.0027	+0.0264	+0.0408
1018	+0.0004 ^e	-0.0003 ^e	+0.0008 ^e	-0.0001 ^e	+0.0008 ^e	-0.0017 ^e	+0.0044	+0.0071	+0.0362	+0.0020	+0.0025	+0.0060	+0.0030	+0.0192	+0.0176
Aluminum Alloys										Run 1	Run 2				
Tens-50	-0.0002	-0.0012	-0.0012	+0.0001	-0.0011 ^f (+0.0004)	-0.0003	+0.0010	+0.0025	+0.0282	+0.0128	+0.0130	+0.0479	+0.0282	+0.0231	+0.0193
2014	+0.0001	-0.0013	+0.0011	0	+0.0002	-0.0004	+0.0009	+0.0028	+0.0131	+0.0075	+0.0072	+0.0245	+0.0156	+0.0114	+0.0106
2024	-0.0004	-0.0005	-0.0011	-0.0002	-0.0004	-0.0005	+0.0004	+0.0022	+0.0138	+0.0056	+0.0098	+0.0126	+0.0138	+0.0063	+0.0050
6061	-0.0005	-0.0039	-0.0007	0	-0.0014 ^f (-0.0001)	-0.0002	+0.0005	+0.0009	+0.0234	+0.0243		+0.0852	+0.0234	+0.0368	+0.0375
7075	+0.0004	0	-0.0002	+0.0002	+0.0004	-0.0002	+0.0012	+0.0017	+0.0102	+0.0096	+0.0075	+0.0390	+0.0203	+0.0150	+0.0154

^aWater content of dry NT0 started below 0.1 weight percent and ended at 0.13.

^bWater content of wet NT0 started and finished at 0.33 weight percent.

^cInitial water content <0.01 weight percent

^dInitial water content 0.22 weight percent

^eWeight changes for metals subjected to these exposures were significantly affected by the specimen rinsing procedure (see text)

^fOne specimen of the four weighed exhibited a large weight loss probably due to weighing error; values in parenthesis are obtained if the apparently spurious specimen is ignored.

TABLE 27

**CORROSION COUPON WEIGHT CHANGE DATA CONVERTED
TO MILS PER YEAR**

Material		Thickness Change, mils per year											
		MS NT0 ⁵			Wet NT0 ⁵			Dry NT0 ⁵ + HF					
		Ambient Temperature		70 C	Ambient Temperature		70 C	Ambient Temperature			70 C		
		1 Month	21 Months	1 Month	1 Month	21 Months	1 Month	1 Month	21 Months	1 Month			
Iron Alloys		+0.0210 ^a	0 ^a	+0.0210 ^a	+0.0420 ^a	-0.0010 ^a	-0.9471 ^a	+0.3066 ^c	+0.0609 ^a	+0.0097 ^c	+0.0019 ^a	+1.9908	+0.40 ^a
304L SS		-0.0420	-0.0010	-0.0210	-0.0420	-0.0010	-1.0710	+0.3066	+0.0609	+0.0122	+0.0024	+2.5515	+0.51
316 SS		+0.0210	-0.0029	+0.0420	-0.0420	-0.0020	-1.1109	+0.5103	+0.1029	+0.0146	+0.0029	+2.8581	+0.57
321 SS		0	-0.0049	+0.0210	-0.0210	-0.0049	-1.5855	+1.1739	+0.2352	+0.0535	+0.0107	+4.4898	+0.90
AM 350		-0.0420 ^e	-0.0431 ^e	-0.3297 ^e	-0.1239 ^e	+0.0029 ^e	-4.5717 ^e	+2.4486	+0.4893	+0.3208	+0.0642	+22.81	+4.56
440C		+0.0819 ^e	-0.0029 ^e	+0.1638 ^e	-0.0210 ^e	+0.0078 ^e	-0.3507 ^e	+2.2449	+0.4494	+0.1725	+0.0345	+18.47	+3.69
1018													
Aluminum Alloys													
Tens-50		-0.1197 ^b	-0.0343 ^b	-0.7203 ^b	+0.0609	-0.0315 (+0.0114) ^{h,f}	-0.1806 ^b	+0.5292 ^d	+0.1953 ^a	+0.0630 ^d	+0.0233 ^a	+14.92 ^d	+5.52 ^a
2014		-0.0609	-0.0372	+0.6615	0	+0.0057	-0.2394	+0.4767	+0.1764	+0.0706	+0.0261	+6.93	+2.56
2024		-0.2394	-0.0143	-0.6615	-0.1197	-0.0114	-0.3003	+0.2121	+0.0777	+0.0554	+0.0205	+7.30	+2.70
6061		-0.3003	-0.1115	-0.4200	0	-0.0400 (-0.0029) ^f	-0.1197	+0.2646	+0.0987	+0.0227	+0.0084	+12.38	+4.58
7075		+0.2394	0	-0.1197	+0.1197	+0.0114	-0.1197	+0.6342	+0.2352	+0.0428	+0.0158	+5.40	+2.00

Material		Thickness Change, mils per year													
		Dry INT0 ⁵						Wet INT0 ⁵							
		Ambient Temperature			70 C			Ambient Temperature			70 C				
		1 Month		21 Months	1 Month		21 Months	1 Month		21 Months	1 Month		21 Months		
Iron Alloys															
304L SS		+0.56 ^c		+0.1113 ^a		+0.0267 ^c	+0.0053 ^a	+0.3066 ^c	+0.0609 ^a	+0.4067 ^c	+0.0810 ^a	+1.0103 ^c	+0.2021 ^a	+8.46 ^c	+1.69 ^a
316 SS		+0.26		+0.0504		+0.0194	+0.0039	0	0	+0.2034	+0.0414	+0.1924	+0.0385	+4.48	+0.90
321 SS		+0.31		+0.0609		+0.0170	+0.0034	+0.1533	+0.0315	+0.3059	+0.0612	+0.6169	+0.1234	+6.22	+1.24
AM 350		+0.92		+0.1827		+0.0851	+0.0170	+1.3272	+0.2646	+1.07	+0.2142	+0.9367	+0.1875	+19.15	+3.83
440C		+1.07		+0.2142		+0.4374	+0.0875	+14.29	+2.86	+1.37	+0.2754	+0.7471	+0.1494	+20.78	+4.16
1018		+1.02		+0.2037		+0.0608	+0.0122	+3.06	+0.6132	+1.53	+0.3059	+0.5434	+0.1087	+8.97	+1.79
Aluminum Alloys															
Tens-50		+6.77 ^d	+6.88 ^d	+2.51 ^a	+2.55 ^a	+1.2071 ^d	+0.4466 ^a	+14.92 ^d	+5.52 ^a	+12.18 ^d	+4.51 ^a	+0.5655 ^d	+0.2092 ^a	+97.56 ^d	+56.10 ^a
2014		+3.97	+3.81	+1.47	+1.41	+0.6174	+0.2284	+8.26	+3.05	+6.01	+2.23	+0.3106	+0.1149	+21.31	+7.88
2024		+3.09	+5.19	+1.10	+1.92	+0.3175	+0.1175	+7.30	+2.70	+3.33	+1.23	+0.1465	+0.0542	+29.64	+10.97
6061		+12.86		+4.76		+2.1470	+0.7944	+12.38	+4.58	+19.40	+7.18	+1.0988	+0.4066	+66.61	+24.65
7075		+5.08	+3.97	+1.88	+1.47	+0.9828	+0.3636	+10.74	+3.98	+7.91	+2.92	+0.4512	+0.1669	+60.12	+22.25

^aThickness of Fe layer equivalent to measured weight change.^bThickness of Al layer equivalent to measured weight change.^cThickness of FeF₃ layer equivalent to measured weight change.^dThickness of AlF₃ layer equivalent to measured weight change.^eChanges for metals subjected to these exposures were significantly affected by the specimen rinsing procedure (see text).^fOne specimen of four weighed exhibited a large weight loss probably due to weighing error; values in parenthesis are obtained if the apparently spurious specimen is ignored.^gWater content data given in Table 26 on page 85.

TABLE 28

SUMMARY OF WEIGHT GAIN RATIO DATA
FROM CORROSION COUPON TESTS

Material	Weight Gain Ratio ^a			
	Dry NT0 + HF	Dry INT0 ^b		Wet INT0 ^c
Iron Alloys				
304L Stainless Steel	1	1		45
316 Stainless Steel	1	1.6		17
321 Stainless Steel	1	1.2		36
AM350	1	1.9		16
440C	2.8	8.6		10
1018	1.6	1.3		6.4
Aluminum Alloys				
		<u>Run 1</u>	<u>Run 2</u>	
Tens-50	2.5	3.7	3.7	
2014	3.1	3.3	3.4	0.9
2024	5.5	2.3	1.3	0.8
6061	1.8	3.5	9.7	1
7075	1.4	4.1	5.2	1

^a Defined as average weight gain after 21 months to the corresponding average weight gain after 1 month

^b Initial water content <0.01 weight percent

^c Initial water content 0.22 weight percent

of the test. The average measured weight changes under various conditions are listed in Table 26. These weight changes are converted to calculated equivalent thickness changes in Table 27. Finally, the calculated weight gain ratios are given in Table 28. Additional observations and a discussion of the test results are presented in the following sections.

MS* and Wet* NT0 Test Results

The 304, 316, and 321 specimens exposed at ambient temperature to MS NT0 were completely unaffected. Those exposed to wet NT0 at ambient temperature showed slight surface discoloration (Table 25). The AM 350 specimens exposed at ambient temperature to wet and MS NT0 were discolored and exhibited about an 0.5 milligram average weight loss between 1 and 21 months of storage (Table 26). The 1018 carbon steel and 440C steel specimens very obviously exhibited both flaking and discoloration. Because of the flaking, the weight changes varied erratically, some specimens exhibiting weight gains and others weight losses. The samples exposed to wet and MS NT0 were dipped successively in 50/50 (v/v) methanol/water, and water, after which the specimens were blotted dry. Some rust was noted on the 1018 carbon steel samples following this procedure.

The 2024 and 7075 aluminum specimens exposed to wet and MS NT0 appeared completely unaffected. The 2014 aluminum specimens appeared visually to be unaffected, but weighing indicated that those specimens exposed to MS NT0 had lost about 1.3 milligrams. The 6061 aluminum specimens also showed no visible damage but they had lost an average of 3.9 milligrams in MS NT0. The Tens-50 aluminum specimens had a roughened surface when exposed at ambient temperature in wet NT0. When the Tens-50 specimens were exposed to MS NT0 at ambient temperature, a 1.2 milligram weight loss was observed. The fact that MS NT0 seems to cause somewhat more corrosion than wet NT0 was unexpected. A possible explanation could be that NT0 reacts with some aluminum alloys to cause weight losses, whereas HNO_3 which is present in the wet NT0, causes the same alloys to gain weight.

*The test solutions are described on page 85.

WGR's are not reported for the wet and MS NT0 tests (Table 28) because the weight gains and losses found after 1 month of storage were only of the order of magnitude of the probable weighing errors; therefore, the WGR values would be meaningless.

In conclusion, when exposed to wet or MS NT0 at ambient temperature for 21 months, 321, 316, and 304 stainless steels, AM 350 steel, and 2014, 2024, and 7075 aluminum exhibited little or no evidence of corrosion, whereas 440C steel, 1018 carbon steel and Tens-50 aluminum in wet and MS NT0, and 6061 aluminum in MS NT0 do exhibit varying degrees of corrosion.

The iron specimens exposed to wet NT0 and the aluminum specimens (except 7075) exposed to MS NT0 at 70 C for 1 month did however, exhibit significant weight losses. Thus, corrosion is a problem at the elevated temperature with all alloys.

Dry NT0* + HF Test Results

The HF content of the NT0 remained above 0.2 weight percent throughout the long-term tests (Table 23).

The 304, 316, and 321 stainless steel and the AM 350 steel test specimens all exhibited extremely light to fairly light coatings. The weight gains of these specimens were, within experimental error, the same after 21 months as they were after 1 month (WGR = 1, Table 28). The 1018 carbon steel specimens had a WGR of 1.6, and the 440C steel specimens had a WGR of 2.8. Because none of the WGR's obtained with the iron alloys even remotely approach 21, it would seem that they are passivating against attack by dry NT0 + HF although some required longer than 1 month (see previous discussion of interpretation of WGR's).

*The test solutions are described on page 85.

All of the aluminum alloys, with the possible exception of 2024 aluminum, seem to fall in the same group as the 440C and 1018 steels. The WGR's of these materials are in the range of 1.4 to 3.1; hence, it would seem that they are passivating against attack by dry $\text{NTO} + \text{HF}$. The 2024 aluminum shows a WGR of 5.5. However, the weight gain (0.4 milligram) measured at 1 month was lower than that found for any other specimens in $\text{NTO} + \text{HF}$, and if the possible weighing error of 0.2 milligram is added to this, a WGR of 3.7 is calculated. In any event, the WGR is still far below 21, indicating slow passivation or a decreasing corrosion rate. Also, the coatings on the 2024 specimens were visually similar to those on the other aluminum specimens. Thus, all of the aluminum alloys also seem to passivate against attack by dry $\text{NTO} + \text{HF}$.

Dry INTO^* Test Results

Although it has been established that added FNO_2 reacts completely with any water present in NTO (as nitric acid), this additive will not be useful unless most metals can be passivated against attack by this fluorine oxidizer when present at 1 to 3 percent in NTO . The remaining coupon tests were run to determine the extent of reaction which occurs in the absence of any special passivation of the metal surface.

The FNO_2 content of the liquids in the test cylinders remained in the INTO range (1 to 3 weight percent) throughout the long-term tests, except that FNO_2 had to be added to the aluminum cylinders at the end of the second month (Table 24).

The 304, 316, 321 stainless steel, and 1018 carbon steel specimens exhibited, within experimental error, WGR's of unity. Little or no coating was visible on the surfaces of the stainless-steel specimens, whereas the 1018 carbon steel specimens were obviously coated with an adherent green layer. For these metals, complete passivation was attained at ambient temperature

*The test solutions are described on page 85.

against the dry INT0 during the first month. AM 350 steel exhibited a WGR of about 2, and thus seems to have passivated during the first few months. 440 C steel on the other hand, showed a WGR of nearly 9. This value is intermediate between a value of 1 for complete passivation in 1 month and 21 for continuous reaction at the same rate for 21 months. Some slowing of the continuous reaction would be expected due to slowed migration of the reacting species through the corrosion layer to the metal surface. Hence, it would seem that 440 C steel had probably not passivated even after 21 months contact with dry INT0.

The 2014, 2024, 6061, and 7075 aluminum specimens all appeared to have a tough and adherent white coating on their surfaces. The toughness and adherence of the layer was quantitatively tested by tapping and scratching the specimens in the dry box in which they were weighed. The Tens-50 specimens had a loose and somewhat flaky layer. Weight changes did not directly confirm the visual observations. WGR's of between 2.3 and 4.1 were found for the specimens. This would indicate that all specimens were passivated. The Tens-50 specimens, which obviously had poor passivation layers, had an average WGR of 3.7. This could be due to the fact that the layer on the Tens-50 specimens was flaking off, thus giving apparently low weight increases.

Wet INT0*Test Results

All of the iron specimens had green coatings and exhibited large WGR's. The coatings were of varying degrees of adherence (Table 25). The 440C steel specimens had a WGR of 10 which would indicate a slowing of the reaction after the first month but probably no passivation. The 1018 steel specimens had adherent coatings and exhibited a lower WGR of 6.4. Based on the results obtained when these two alloys were exposed to dry INT0, where WGR's of 8.6 for 440 C steel and 1.3 for the 1018 steel were obtained, it seems likely that the 1018 steel was finally passivated.

*The test solutions are described on page 85.

The three stainless-steel specimens and the AM350 specimen had WGR's of from 16 to 45. The values over 21 can only indicate a speeding up of the reaction after an initial month of storage. A possible explanation would be that these specimens were protected from initial reaction with the FNO_2 by their resistant oxide coatings and then, once the coatings had been eaten through, the reaction proceeded more quickly with the metals themselves. If this is true, then the WGR's obtained for these materials are indeterminate because once the oxide coating was pierced, passivation could have occurred within a short time or a continuous reaction could have proceeded. The average weight gain over 21 months for these four alloys was 24 milligrams as compared to weight gains of 26 milligrams for 440 C steel and 19 milligrams for 1018 carbon steel.

The aluminum specimens all showed WGR's of approximately 1 over the 1- to 21-month period. Visual examination of the coatings, plus tapping and scratching them in a dry box, indicated that they were of a slightly looser nature than those present on the specimens exposed to dry INT0. A subjective rating of the coatings, from most to least adherent, would be 6061 > (2014, 2024, 7075) > Tens-50, the three alloys in parentheses being essentially equal. The coatings on specimens exposed to the vapor phase were adherent, except in the case of the Tens-50 alloys. The fact that the WGR's for these specimens were somewhat lower than the corresponding WGR's for the specimens exposed to dry INT0 is probably due to some loss of the less adherent coatings.

SUMMARY OF COUPON CORROSION TESTS

304, 316, and 321 Stainless Steels and AM350 Steel Alloy

1. The alloys are not significantly affected by either wet or MS NT0 during 21 months at ambient temperature.
2. Wet NT0 but not MS NT0 significantly corrodes these alloys at 70 C during 1 month's exposure.

3. The alloys are essentially passivated against attack by dry NT0 + HF after 1 month at ambient temperature.
4. The alloys are essentially passivated against attack by dry INT0 after 1 month at ambient temperature.
5. It is indeterminate from the data whether these alloys passivate at ambient temperature against attack by wet INT0.

440C Steel Alloy

1. This alloy is significantly attacked by both wet and MS NT0 during 21 months at ambient temperature.
2. Wet NT0 very significantly attacks this alloy in 1 month at 70 C.
3. MS NT0 also significantly attacks this alloy in 1 month at 70 C.
4. The alloy passivates against dry NT0 + HF at ambient temperature.
5. Passivation against dry or wet INT0 probably does not occur.

1018 Carbon Steel Alloy

1. This alloy is significantly attacked by both wet and MS NT0 during 21 months at ambient temperature.
2. Wet NT0, and to a lesser extent MS NT0, significantly attacks this alloy at 70 C during a 1 month exposure.
3. The alloy passivates against dry NT0 + HF at ambient temperature.
4. The alloy passivates against dry INT0 after 1 month at ambient temperature.
5. After several months, the alloy seems to passivate against wet INT0.

2014 Aluminum Alloy

1. This alloy is slightly attacked during 21 months at ambient temperature by MS NT0 but not by wet NT0.

2. Neither wet nor MS NT0 significantly affects this alloy during 1 month at 70 C.
3. The alloy passivates against dry NT0 + HF after somewhat more than 1 month of storage at ambient temperature.
4. After a few months at ambient temperature, the alloy seems to passivate against dry INT0.
5. The alloy passivates against wet INT0 after 1 month at ambient temperature.

2024 Aluminum Alloy

1. This alloy is unaffected by wet or MS NT0 during 21 months storage at ambient temperature.
2. MS NT0, and to a lesser extent wet NT0, significantly attacks this alloy in 1 month at 70 C.
3. The alloy passivates against dry NT0 + HF somewhat more slowly than do the other aluminum alloys tested.
4. The alloy passivates against dry INT0 somewhat more quickly than do the other aluminum alloys tested.
5. The alloy passivates against wet INT0 after 1 month at ambient temperature.

6061 Aluminum Alloy

1. MS NT0 significantly attacks this alloy during 21 months at ambient temperature.
2. MS NT0, but not wet NT0, slightly attacks this alloy in 1 month at 70 C.
3. The alloy passivates against dry NT0 + HF after somewhat more than 1 month of storage at ambient temperature.

4. After a few months at ambient temperature the alloy seems to have passivated against dry INT0.
5. The alloy passivates against attack by wet INT0 after 1 month at ambient temperature.

7075 Aluminum Alloy

1. This alloy is unaffected by wet or MS NT0 during 21 months at ambient temperature.
2. The alloy is unaffected by wet or MS NT0 during 1 month at 70 C.
3. The alloy passivates against dry NT0 + HF after somewhat more than 1 month of storage at ambient temperature
4. The alloy seems to passivate against dry INT0 during a few months at ambient temperature.
5. The alloy passivates against wet INT0 after 1 month at ambient temperature.

Tens-50 Aluminum Alloy

1. This alloy exhibits a slight weight loss and a roughened surface after 21 months' exposure to wet NT0 at ambient temperature.
2. MS NT0, but not wet NT0, slightly attacks this alloy in 1 month at 70 C.
3. The alloy passivates against dry NT0 + HF after somewhat more than 1 month of storage at ambient temperature.
4. This alloy does not passivate against attack by either dry or wet INT0.

Additional Observations

Wet and MS NT0. No differences were observed between the coupons stored in contact with the propellant vapor and those in contact with the liquid. Welded and nonwelded specimens were similarly affected.

Dry NT0 + HF. The specimens exposed to the vapor phase generally exhibited larger weight changes than those exposed to the liquid phase. This trend was more pronounced with the aluminum alloys. No differences were noted between welded and nonwelded specimens.

Wet INT0 and Dry INT0. The specimens in contact with liquid generally exhibited slightly larger weight changes than the corresponding vapor phase specimens. This trend also was more pronounced in the aluminum tests. No differences were noted between welded and nonwelded specimens.

CONCLUSIONS

The presumption of gross corrosion occurring to metals exposed to wet NT0 has been conclusively disproven. The results of the long-term (21 month) corrosion tests described herein indicate that the actual corrosion rates with wet NT0 are far smaller than previously reported, and do not differ from those obtained with MS NT0 for most metals. The reason for this difference in measured corrosion rates between this and previous programs is traceable to the difference in the duration of the tests.

The calculation of a mils per year rate from a 1-week test consists of determining the change in mils and multiplying by 52 on the assumption that the rate will remain constant over the longer period. The long-term tests carried out on this program prove that in the case of NT0 "corrosion" the rate of change in mils drops off drastically after a short period of exposure.

Several of the metals studied seem to passivate well against attack by the FNO_2 and HF in INT0. This suggests that practical passivation techniques could have been developed for this oxidizer system had the long-term results verified the general presumption that wet NT0 is a highly corrosive liquid with most metals.

The 30-day tests at 70 C indicated that MS NT0 was less corrosive than wet NT0. Most of the experimental data had been obtained under the three INTO programs before the results of 21-month tests showed that neither wet nor MS NT0 is particularly corrosive at ambient temperature.

TASK II: SMALL BOMB STORABILITY,
CONTRACT AF 04(611)-10809

INTRODUCTION

One of the primary purposes of the INTO program was to select the most suitable fluorine oxidizer to add to NT0. Both F_3NO and FNO_2 seemed likely candidates because: (1) either would react with HNO_3 , (2) neither should affect the propellant properties, and (3) both would allow a high proportion of fluorine loading for a relatively small increase in vapor pressure. As a result of storability tests previously reported (Ref. 5), F_3NO was eliminated as a possible additive because it was found that it would react with N_2O_4 to form FNO_2 . The continuation of the tests previously reported for a 21- to 25-month period has confirmed the storability of FNO_2 - N_2O_4 mixtures in containers of 321 SS, 6061 Al, and nickel. Other tests have indicated that INTO is also storable for short times at 130 C.

EXPERIMENTAL

FNO_2 -NT0 mixtures prepared as previously reported (Ref. 5) were stored in 10-milliliter bombs of 304L SS, 321 SS, 6061 Al, and nickel. The bombs were stored at 70 C and at ambient temperature in a valve down position for periods of 21 to 25 months. The contents of the bombs were analyzed periodically by infrared spectrometry to determine their FNO_2 concentrations. Short-term (24 hour) storability tests were also run at 130 C.

RESULTS OF DISCUSSION

The results of the 70 C and ambient temperature tests are given in Table 29. All bombs started out with 3 weight percent FNO_2 . The two aluminum bombs stored at ambient temperature apparently passivated during the first 2 months. The 70 C bombs were reloaded after 6 months because all of the liquid had been used up in sampling. The 70 C stainless-steel bomb was reloaded again after 15 months of storage with NT0 containing 16 weight percent FNO_2 . This FNO_2 concentration was used because the solution

TABLE 29

70 C AND AMBIENT TEMPERATURE STORABILITY DATA,
10-MILLILITER TEST CYLINDERS

Cylinder Material	Temperature	Initial Water Content weight percent	FNO ₂ Content (weight percent) at Various Times (months)											
			0	2	3	4	7	9	12	15	17	18	21	25
Aluminum 6061	70 C	0.2	3	3	3	3	3	(3) ^{a,b}	3	2		3	2	3
	Ambient	0.08	3	0(3) ^b					3		2		3	
	Ambient	0.2	3	0(3) ^b					2		1		2	
Stainless Steel 321	70 C	0.2	3	3	3	3	3	(3) ^{a,b}		0.4(16) ^b		3	3	2
	Ambient	0.08	3	2				3		3		2		
	Ambient	0.2	3	3				2	3	2		2		
Nickel	70 C	0.2	3	3	3	3	3	(3) ^{a,b}		3		3	4	4

^aAll of the INT0 had been used up in sampling

^bThe bombs were reloaded with INT0 containing the amount of
FNO₂ shown parenthetically

was available from another task. The FNO_2 content of this solution levelled off in the INTO range.

The results at 70 C and ambient (Table 29) indicate that INTO is storable in these metals.

The results of the 130 C tests are given in Table 30. INTO is sufficiently stable under these conditions that it should survive a sterilization procedure.

CONCLUSIONS

INTO is storable and may be used with 304L SS, 321 SS, 6061 Al, and nickel when the containers are sufficiently passivated.

TABLE 30

130 C STORABILITY DATA, 10-MILLILITER
TEST CYLINDERS

Cylinder Material	FNO ₂ Content (weight percent)		
	Initial	24 Hours	48 Hours
6061 Aluminum	12	8	4
321 Stainless Steel	6	6	5
Nickel	8	4	4

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APPENDIX: METAL ION ANALYSES IN NT0--DETAILED PROCEDURE

DIRECT HYDROLYSIS METHOD

PROCEDURE

Transfer approximately 10 milliliters (ml) of NT0 propellant directly from NT0 samples into a 10-ml graduated cylinder. Record exact volume of NT0 in the 10-ml graduate. Pour contents of 10-ml graduate into a 100-ml graduated cylinder containing 40 ml of frozen deionized water. Cover the graduate with a small inverted beaker and allow the contents to warm slowly to room temperature. Secure the cylinder containing the sample in a hot water bath (~90 C) and allow it to remain in the bath until the solution becomes one phase and vigorous bubbling ceases. Allow it to cool to room temperature and record the liquid level in the graduate. Transfer the hydrolyzed solution to a glass-stoppered flask which is suitable for subsequent atomic absorptions analyses.

The samples along with the standard are run on a Perkin Elmer Atomic Absorption Spectrometer 303 or equivalent for the metals of interest. The standards are made up in 10-percent nitric acid to simulate the hydrolyzed NT0 samples

A standard curve of parts per million of metal (ppm or micrograms per milliliter) versus absorbance is plotted for each metal. From these curves, concentration of the metals in the NT0 hydrolyzate is read directly in ppm and is converted to concentration in the original NT0 as follows:

$$\text{ppm of metals in NT0} = \frac{\text{ppm metal in hydrolyzate} \times \text{vol. of hydrolyzate (ml)}}{\text{vol. of NT0 (ml)}}$$

REAGENTS

1. Atomic Absorption Standards for each metal of interest, Scientific Products, Burbank, Calif., or equivalent
2. Nitric Acid, Reagent Grade, J. T. Baker, Phillipsburg, N. J.
3. Deionized H₂O

TWENTY-FOLD EVAPORATIVE CONCENTRATION OF NT0

When increased sensitivity is needed for the elements being determined, the following procedure describes an evaporative concentration step that is carried out prior to hydrolysis of the NT0.

A 100-ml centrifuge tube is placed on the NT0 sampling line (Fig. A-1). All ball joints and O-rings on Fischer-Porter valves are lubricated with a minimum amount of silicone grease. The manifold and centrifuge tube up to the NT0 sample are evacuated. One-hundred ml of NT0 is then allowed to flow into the centrifuge tube. The Fischer-Porter valves on the NT0 supply and on the centrifuge tube are closed and the excess NT0 is pumped into the -78 C trap. The Fischer-Porter valve on the centrifuge tube is partially opened and the NT0 is carefully allowed to evaporate and condense in the -78 C trap until 5 ml of NT0 remain. The 5-ml NT0 residue is then hydrolyzed and analyzed as described in the analysis procedure above using 20 ml of frozen deionized water rather than 40 ml. The ppm metal is calculated as follows:

$$\text{ppm in NT0} = \frac{\text{ppm in hydrolyzate} \times \text{vol. of hydrolyzate (cc)}}{\text{Volume of NT0 (ml)} \times 20}$$

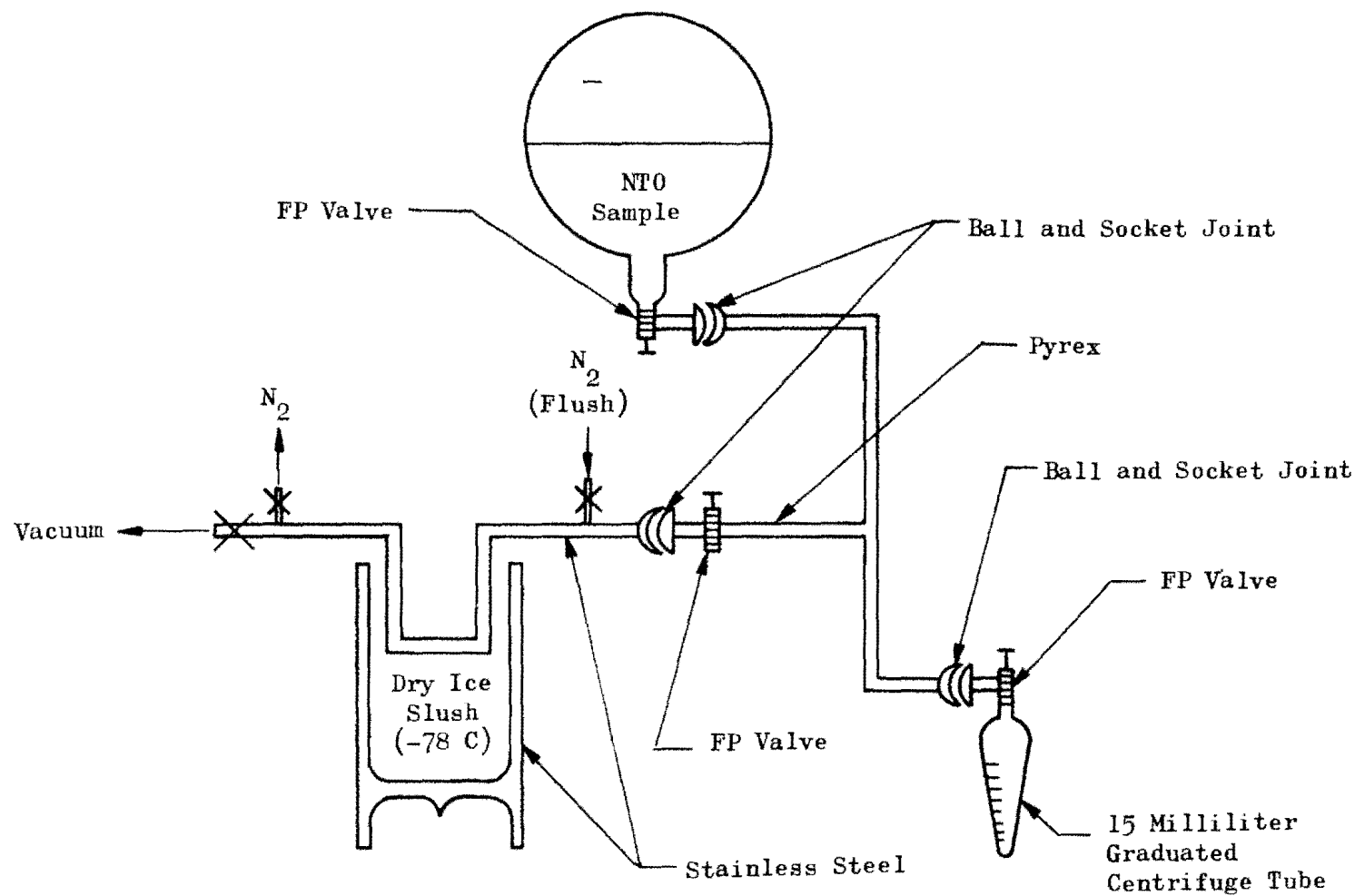


Figure A-1. System for Evaporative Concentration

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13. ABSTRACT The results are presented for three programs which were conducted to further develop and characterize "inhibited N_2O_4 " (INT0) which is N_2O_4 containing 1 to 3 weight percent $FN0_2$. The purpose of the fluorine oxidizer is to react with any water which might intrude into the propellant. Long-term corrosion tests were also conducted with "wet" and dry NT0. Stress corrosion tests were conducted with the two current propellant-grade NT0's, MIL-P-26539 and MSC-PPD-2A.			

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